

Final Report

Grant NAG-1-1918

Collection and Analysis of Aircraft Emitted Particles

Submitted 30 September 1999

by

James Charles Wilson, Principal Investigator
Department of Engineering
University of Denver
Denver CO 80208-0177

Abstract

The University of Denver Aerosol Group proposed to adapt an impactor system for the collection of particles emitted by aircraft. The collection substrates were electron microscope grids which were analyzed by Dr. Pat Sheridan using a transmission electron microscope. The impactor was flown in the SNIFF behind aircraft and engine emissions were sampled. This report details the results of that work.

Impactor System

We built an impactor system which collected particles in the aerodynamic diameter range from 10 nm to 100 nm. The collection substrate was an electron microscope grid which permitted analytical electron microscopy to be done on the collected particles. The aircraft inlet was supplied by NASA Langley as was the pressure control valve and pump. The pressure reducer consisted of an orifice and a chamber of such dimensions that particles in the 0.01 to 0.1 μm range were not lost to the walls. The pressure control valve and pump maintained the pressure in the chamber at 44 mb at all aircraft sampling altitudes. The flow into the pressure reduction chamber was approximately 0.25 standard liter per minute (SLPM). The pre-impactor removed particles larger than 0.1 μm . The impactor flow control maintained the required sample flow of 50 cc/s through each of the impactors when they were sampling. The by pass valve permitted the flow control circuit to function continuously. Since the response time of the controller is long, we wanted the flow to be established and constant.

The impactor was controlled in flight by three switches. One advanced the carousel from one sample to the next. The second initiated sampling and the third provided power to the system. A switch box was provided so that the operator could control the system from a seat at some distance from the assembly.

The impactor system included of the following components:

- Impactor wheel containing 24 sample collection stages. One is usually used for a blank.

- Stepper, stepper controller and stepper driver to move the wheel. Drive train.

- Pressure reducing orifice and chamber designed to pass particles in the 10 to 100 nm diameter range. Pressure will be reduced from ambient levels to about 40 mb. The pump and pressure controller required to do this were provided by NASA Langley. DU provided an absolute pressure sensor.

- Pre-impactor designed to remove particles larger than 100 nm in diameter from the sample stream. These particles are removed upstream of the collection impactors. DU provided a pressure sensor to measure pressure drop across the pre-impactor.

- Impactor flow control system consisted of :

 - Pump in a sealed can so that leaks through bearings do not confound flow measurement

Flow control circuit
Laminar Flow element with pressure sensor
By-pass valve and flow resistance. Solenoid controlled valve to choose sample or by pass.
Power Supply.
Box to contain system
Control box to permit the operator to turn on the system, advance the sample wheel to the next sample and start and stop sampling.
Analog outputs for pressure, pressure drop across the pre-impactor, flow through the impactor and temperature (6 total). Langley recorded these data.

The impactor system was installed in the NASA Langley aircraft by a University of Denver Research Engineer.

Analysis of Collected Samples

Pat Sheridan analyzed the samples on the electron microscopic grids with a NIST 200 kV STEM at Boulder. His report is attached to this report.

Summary of Analysis and Conclusions

Aircraft exhaust particles were observed in a variety of morphologies ranging from classic chain aggregate soot particles to 'amorphous blob' particles that may have impacted in a wet, moist or dual-phase state. Some samples showed blob particles that looked like they have been coated chain aggregates. Regardless of their morphology, all the carbon containing particles had similar xray spectra and showed C, O and Si.

Measurements were made behind an F-16 and a C-130 aircraft. Although the composition of the carbon containing particles were similar in plumes from the two planes, the morphological characteristics of the samples differed. The F-16 particles contained a higher fraction of solid and chain aggregate soot particles and the C 130 showed more blob-like particles.

Reporting of Results

These results were reported at the American Geophysical Union Fall Meeting in 1997 and a manuscript will be submitted to Geophysical Research Letters within a month.

CHARACTERIZATION OF AIRCRAFT EXHAUST PARTICLES SAMPLED DURING THE
NASA SASS/SNIF III PROGRAM USING ANALYTICAL ELECTRON MICROSCOPY:
REPORT OF ANALYSIS

Patrick J. Sheridan, Ph.D.
Electron Microscopy Consultant
3305 Darley Avenue
Boulder, CO 80303
303-494-1461

Final Report of Analysis

12 December 1997

Summary. Twenty aerosol samples were collected in aircraft exhaust plumes on coated electron microscope grids using a low-pressure impactor mounted on a NASA chase aircraft. Two additional samples were collected in background air at the same altitudes that exhaust samples were collected. The samples were then analyzed to determine the morphology, chemical composition, and relative abundance of individual particles using analytical electron microscopy.

Analysis of all of the samples permits the following generalizations to be made concerning particle distributions in aircraft exhaust. First, exhaust particles emitted from the two different types of source aircraft often showed different morphologies, with the C-130 aircraft exhaust particles usually resembling amorphous "blobs" or coated soot particles and the F-16 particles (at least those collected close to the source aircraft) most often appearing as classic chain aggregate soot. The elemental composition of both types of particles was essentially the same (major C, with minor O and Si), but the relative amount of organic C present could not be determined and may have varied widely. The presence of Si in most exhaust soot particles from all samples is interesting and may be an effect of the use of Si-containing fuel additives or lubricants in the engines of military aircraft. Second, some samples collected closely behind the C-130 aircraft showed particles and other features that were difficult to view clearly. We have speculated on the presence of a coating or film either on the particles before sampling or deposited to the grids during impaction. These coatings, if present, do not contain appreciable S and appear to be of similar elemental composition as the particles. Darker spots (perhaps residues) surrounding most particles in these samples support this possibility. Questions are raised in this report regarding the operation of the impactor, particularly in the observation of uneven deposition patterns and the sampling of background air.

CHARACTERIZATION OF AIRCRAFT EXHAUST PARTICLES SAMPLED DURING THE
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Table Of Contents

Summary.....	i
Table of Contents.....	ii
I. Introduction	1
II. Description of the Analytical Methods.....	1
A. Capabilities and limitations of the analytical electron microscopy system.....	1
B. Analysis strategies.....	2
III. Analysis Issues.....	3
A. Grid handling	3
B. Sample peculiarities (uneven deposits)	4
IV. Variability of the Aerosol Samples Related to Aircraft Type, Fuel, Separation, etc.....	5
V. Characterization of Individual Samples.....	7
VI. Discussion.....	22

I. Introduction

This document has been structured in a "Report of Analysis" format. In this format, detailed accounts of the analyses of individual aerosol samples collected by NASA aircraft are presented, along with any problems encountered during these analyses. Detailed discussion of the analytical methods are presented, so that all Principal Investigators have this information and can suggest changes in the techniques if deemed necessary. Speculation on the causes of potential sampling problems is offered, and questions are put forth to elicit thought on how to overcome these problems and to help decide which data, if any, are invalid. This detailed report is for the use of the Principal Investigators and was not meant to be a public document, although it contains the essential results of the electron microscope analyses and with editing could serve as a template for future papers.

II. Description of the Analytical Methods

A. Capabilities and limitations of the analytical electron microscopy system

The microanalysis of all aerosol samples was performed using the NIST/Materials Reliability Division 200 kV analytical electron microscope. Time is scheduled for microscope use in advance and hourly user fees are assessed to cover the costs of expendable supplies (primarily electron gun filament replacement, photomicrograph film and darkroom supplies, and liquid nitrogen). The typical rate is around \$100 per hour for approved users.

The NIST instrument is a JEOL 200CX analytical electron microscope equipped with two energy-dispersive x-ray spectrometers. The microscope has sufficient resolution in the standard viewing (i.e., transmission) mode to detect solid particles smaller than 0.01 μm in diameter. The x-ray detectors permit the collection of x-ray spectra from individual or aggregate particles that represent their elemental composition. The particle size limit for x-ray analysis of solid particles is variable and depends on which elements are present and the mass fraction of these elements, but in practice ranges between ~ 0.05 and 0.1 μm diameter.

The minimum sizes for viewing and analyzing acidic sulfate particles are larger than for solid particles. This is primarily due to two effects. First, impacted H_2SO_4 droplets that are not fixed in some way (e.g., by ammonia or evaporative coating) spread out on the formvar film to a larger diameter than the particles exhibited in the atmosphere, and this spreading decreases the viewable contrast between film and particle. Second, water is lost in the high vacuum environment of the transmission electron microscope (TEM), so that instead of viewing a hemispherical cap we are viewing a relatively flat S-containing residue or spot. Both of these effects combine to make small H_2SO_4 droplets difficult to view in the electron microscope. In practice, S-containing spots down to ~ 0.05 μm are visible during the analyses. We typically do not expect to be able to get a usable x-ray spectrum from a particle with such little mass. Particle morphology, contrast and instability in the electron beam allow classification of these particles nonetheless. The lower size limit for obtaining an x-ray spectrum identifying the particle as S-containing is closer to 0.1 μm .

The obvious question to ask here is how the size of the analyzed H_2SO_4 particle relates to the size of that particle in the atmosphere. We have not performed laboratory studies to answer that

question yet, although others have. While the works we have found differ in the relationship between impacted and true particle size by several hundred percent, it seems clear that particles in the atmosphere display smaller spherical diameters than the diameters of the circular acid spread spots. What is unknown is whether true atmospheric particle diameters are 75%, 50% or 25% of the spread spot diameters. What is likely is that a 0.05- μm diameter H_2SO_4 particle viewed in the TEM had a substantially smaller pre-impaction diameter.

B. Analysis strategies

The analysis of particles on a typical 200-mesh copper TEM grid with a formvar film coating occurs in three stages and usually takes 4-5 hours. In the first stage, the grid is observed at a lower magnification (e.g., 1,000X) to determine if a central aerosol deposit (CAD) is present. A CAD is usually not located in the geographic center of the grid; its location depends on the positioning of the grid on the impaction surface. A cross section of the deposited particle number density across a typical CAD is roughly Gaussian in shape, with particle loadings falling off dramatically with distance from the center of the deposit. Figure 1 is a drawing that depicts a typical central aerosol deposit on a 200-mesh TEM grid. Note that for a 200-mesh grid, each square is $\sim 80\text{-}100\ \mu\text{m}$ across and that this field-of-view (FOV) covers only a few percent of the total grid area. The grid extends for several FOV diameters outward in all directions from here, and after moving out one diameter (~ 6 squares) in any direction from this location, observed particle numbers are much lower. Upon finding the CAD region, observations regarding its areal extent, the relative particle loading, the major observed particle types, and any peculiarities in the aerosol deposits (e.g., deposition inhomogeneities) are made. Photomicrographs of FOVs in different areas of the grid are often taken at this time.

Experience in analyzing the aerosol deposits from this impactor tells us that CADs are to be expected when the impactor is functioning properly (e.g., no system leaks, particle bounce effects or impactor jet clogging). It is our opinion that the lack of a CAD suggests either (1) the grid was positioned well off center on the impaction surface or (2) the impactor was not functioning properly.

The second stage of grid analysis involves obtaining information on individual particles from over the entire grid area. Since studies have shown that particles of different aerodynamic diameter are likely to deposit at different radial distances from the impactor jet and since particle type may well be related to aerodynamic diameter, we have chosen to analyze areas on the grid at different radial distances from the central deposit. This ensures that a more representative sampling of particles is obtained than if only one grid area was analyzed. In these analyses, particles are randomly chosen and analyzed for elemental composition using the x-ray spectrometer system. Particles are classified according to major detected elements, or in some cases, according to interesting trace element chemistry. Generally, at least one representative x-ray spectrum of each major particle type present in the sample is archived. Notes are kept that describe the appearance and size of the particle that produced each archived spectrum. Generally, 10-20 spectra of these "typical" analyzed particles are saved during a grid analysis. Often, particle types are observed that already have an archived spectrum. In these cases, after collecting the x-ray spectrum for a period of time sufficient for particle classification, the spectrum is discarded and a new analysis begun. In this manner, an impressive number of particles can be analyzed for elemental composition in a relatively short time, and an overall

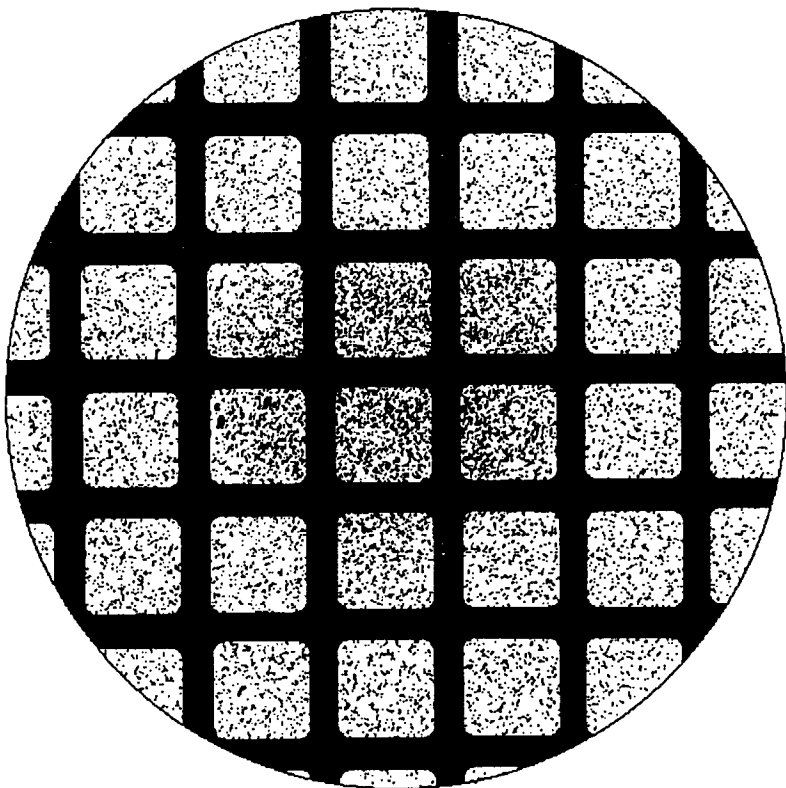


Figure 1

impression of the distribution of particle types is obtained before the formal particle counting procedure (described below) is started.

The transparent C-coated formvar films used to support the collected particles contain C and O in small but detectable amounts. The films contain major mass fractions of C, but relatively little C mass since they are so thin. A small Si peak is observed in most x-ray spectra due to fluorescence of the Si dead layer inside the detector. Thus, the C, O and Si peaks from analyzed particles all contain contributions from the thin film or the detector. These system background contributions are determined by collecting several spectra from particle-free areas on the thin films on each grid. These background spectra are averaged for each sample, and the average system background contribution for each element calculated. These are usually small compared with the elemental contributions from a typical aircraft exhaust particle of sufficient size, and are subtracted from the total (particle + system) x-ray spectrum for each analysis.

The final stage of grid analysis involves the counting and classification of 500 particles. This procedure has been described in more detail in our previous publications. Briefly, the microscope magnification is increased to 20,000X and a square containing particles near the CAD region is selected for analysis. At 20,000X, solid particles less than 0.02 μm in size are visible during the analysis. Depending on the loading of particles in the grid square, one or more traverses across the square are made. All particles that pass within the boundaries of a small rectangle on the viewing screen during the traverse are counted and classified. This involves determination of the morphology and elemental composition of each particle $>0.05 \mu\text{m}$. Upon completion of a traverse, particle types are tallied and, depending on the loading, another traverse is begun either within the same grid area or in another portion of the grid. As stated above, traverses are performed in areas of the grid at several different radial distances from the impactor jet. Typically, x-ray spectra and photomicrographs of the analyzed particles are not archived during this analysis stage due to instrument use constraints, unless a new particle type or otherwise interesting particle is encountered.

III. Analysis Issues

A. Grid handling

A couple of issues that could be preventable caused problems with the TEM grid analyses. First, of the twenty-two samples sent for analysis, several grids were badly mangled nearly to the point of being unusable. The grids were straightened and flattened as well as possible with microforceps, but viewing under the electron microscope revealed many broken films over grid squares, as well as broken grid bars in some samples. This of course limited the viewable (i.e., intact-film) area, to in some cases as little as 10-20% of what it normally is in a well-handled specimen. Since the surface of the grid was not flat on a microscopic scale, analysis was slowed considerably because movement from one particle to the next generally meant that the new focus was off, even within the same grid square. In two cases, the double-stick tape used to secure the grid to the impactation substrate was sticking to part of the grid, making this area unusable for analysis. Every investigator that works with these tiny grids in a field setting is well aware of the handling difficulties and has probably ruined a few grids. The point of this discussion is not to trivialize those difficulties, because they are significant, but to restate this important point. Extra care taken in the field handling of grids translates to potentially more information available in the

microanalysis of the aerosol sample.

Another issue that limits the analytical capabilities of the techniques we employ is the use of TEM grids of a smaller mesh size. We suggest that only 200-mesh Cu TEM grids with a formvar/carbon film be used for aerosol collection. There are many other grid materials, meshes, and films available, but many years of experience have given us confidence that our suggested grids are the best for our purposes. In Figure 1, the relative viewable film-to-grid bar area is approximately accurate in this depiction of a 200-mesh grid and is 60-70%. That gives plenty of impaction substrate to analyze. Compare this with Figure 2, which is a drawing of one of the smaller-mesh (probably 400-mesh) grids used in about half of the samples in this study. Relative to a 200-mesh grid, the size of a 400-mesh grid square is reduced in both dimensions by a factor of 2 (~80 μm to ~40 μm), and the viewable area reduced a factor of 4. This means that even in a well-handled grid with no broken films, only ~15% of the grid area is available for viewing, and all of these smaller-mesh grids showed at least some film breakage. We strongly suggest that 200-mesh TEM grids be used in future studies.

B. Sample peculiarities (uneven deposits)

One disturbing observation was made in a number of the samples. In these samples, the particulate deposit did not resemble the expected CAD with particle loadings decreasing from a central high-density region. Instead, small "deposition islands" of high particle number density were spread around the grid. The areal extent of most of these islands was relatively small; generally one or two grid squares. Squares adjacent to these usually showed low particle numbers. Figure 3 illustrates this situation. Another figure later in this report shows a photomicrograph of the deposition islands.

The morphology of particles in these small, high-loading islands was often different than in samples where no islands were found. The classic chain aggregate soot particles were typically absent, and a more compacted deposit was visible. The composition was very similar to the chain aggregate soot analyzed throughout this study – typically major C with O and Si, although often the Si was present in higher mass fractions in these deposits. We believe that these island deposits are essentially the same material present on the other grids, we just question how it got there.

Actually, several questions require answers regarding the uneven deposits on these grids. The obvious question is "What caused these uneven deposits?" It is unlikely that large agglomerate particles happened to bypass the pre-collection surface and impact on just a few chosen grid squares. One possibility is particle bounce-off from the pre-collection substrate that was designed to remove larger particles from the collected sample. If the particulate deposit built up to a point where ablation could occur, relatively large, moist, compacted chunks of the deposit could be ejected back to the collection substrate. This could explain why adjacent squares often showed orders of magnitude differences in observed particle loadings. This effect also was observed more frequently in samples from later in the program, which would be consistent with a build-up problem.

Another question to raise is "Was there an impactor malfunction when these deposits were formed that precluded the collection of a representative sample?" Most of the time samples that displayed the "island" type of deposits did not also show a CAD region. One would think even

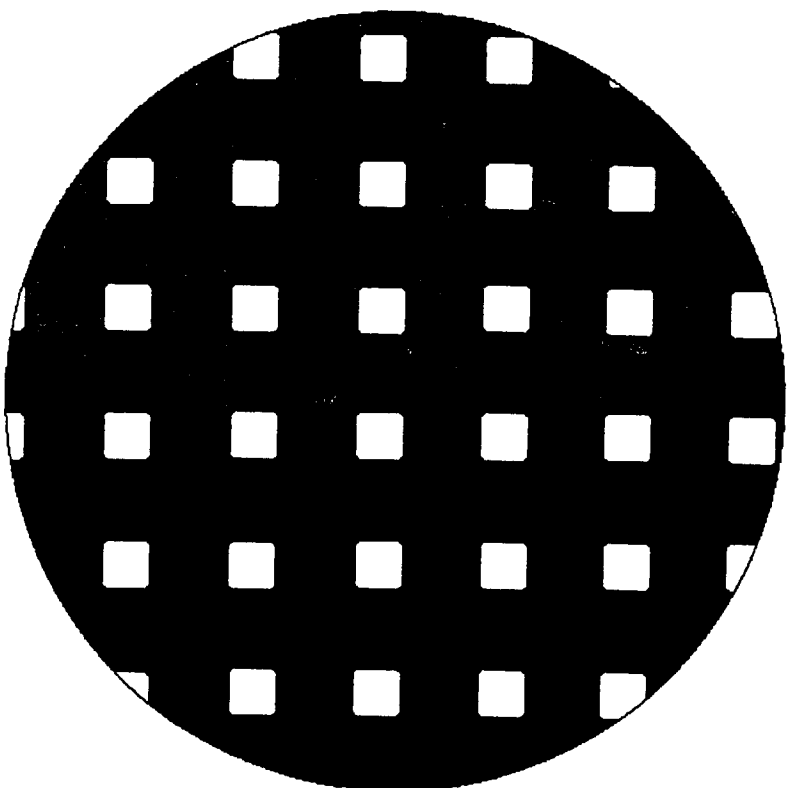


Figure 2

if clumps were breaking off the pre-collection surface, that small particles would still follow the streamlines around to the collection substrate to form a CAD. This was, however, usually not the case. Some of the aerosol deposits were quite heavy, signifying very high concentrations of aerosol particles being sampled. Could the deposit have grown over time to a sufficient size to influence (or even block) the flow streamlines? Could there have been a leak or pressure change within the impactor during these samples that changed the cut size or introduced contamination?

These questions are being raised here to elicit thought on whether all or only some of the samples are usable for us to talk about in reports and papers, and just how we want to go about determining which samples are usable. For now, we view these samples as suspicious and will attempt to determine just how much usable information they contain. For example, the 500-particle classifications may still be representative if the traverses are performed in areas of the grid removed from the island deposits. In a later section of the report we will describe each sample in detail.

IV. Variability of the Aerosol Samples Related to Aircraft Type, Fuel, and Separation

The elemental composition of aircraft soot was fairly consistent no matter which of the two aircraft (F-16 or C-130) or several types of fuel was generating it. Aircraft soot particles were composed mostly of C, usually with trace-to-minor amounts of O and Si and occasionally trace S present. Figure 4 shows x-ray spectra from five very small soot particles from an F-16 exhaust sample (JP-8 fuel, 0.05 nautical miles separation distance) superimposed on two system background spectra. Peak areas of C and Si in the soot spectra are generally observed to be several times larger than the system background contributions, with O only slightly above background. In this x-ray system, C x-rays are detected far less efficiently than are Si x-rays, so relative background-subtracted peak heights do not translate directly into elemental mass fractions in the particles. Silicon is present at the one-to-few percent level in most of these particles. Sulfur peaks were not observed in these particles, and should have been easily detected if present because there is essentially no system background for S. Sulfur was, however, present in detectable amounts on a minority (~5-20%) of the soot particles in this and other JP-8 fuel exhaust samples. In the one analyzed F-16 exhaust sample where Low-S fuel was burned, no CAD region was found and extremely inhomogeneous deposits were encountered. Individual particles were relatively rare and an impactor malfunction was suspected. X-ray analyses of the particles present indicated the C-O-Si composition with relatively few particles showing detectable S. The occurrence of Si in aircraft soot particles has not to our knowledge been observed previously, and might be useable as a marker to distinguish aircraft-generated soot from other types of C-rich particles in the atmosphere.

The fraction of soot particles containing detectable S increased in exhaust samples from aircraft burning High-S fuel. For definition purposes we will define "detectable" as the minimum elemental mass necessary to create an observable disturbance in the x-ray continuum at the energy of interest. Perhaps a better phrase to use would be "barely detectable". It must be noted that this is not a robust definition of the amount of material present, and is less than our usual definition of "trace", which is generally less than a few percent by weight but clearly above background. Particles classified as "C-O-Si, with S" in the next section of this Report showed S clearly above the system background, and generally were present in smaller number fractions than the particles with "detectable" S. Our detection limit is based on elemental mass, so a S

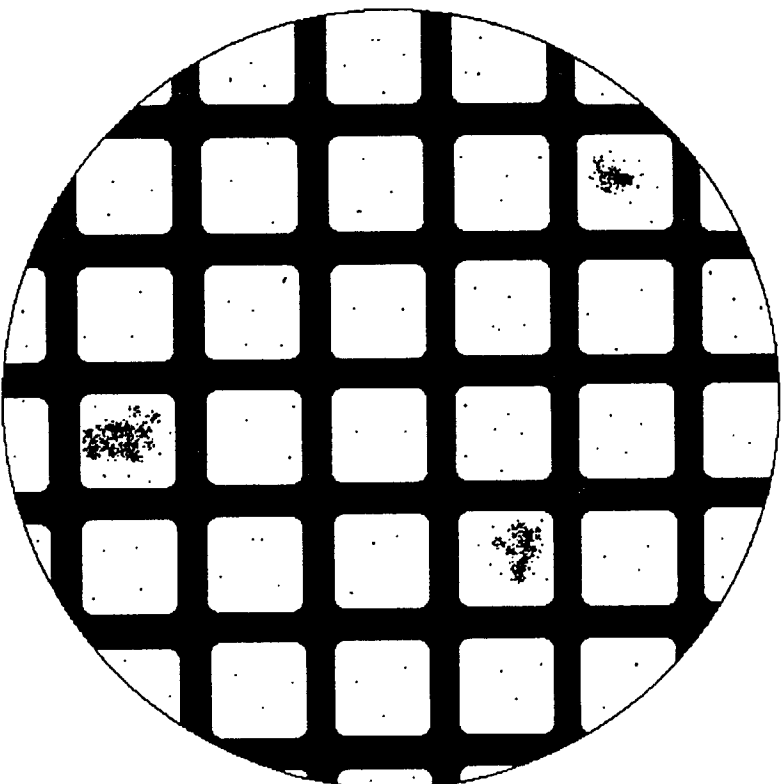


Figure 3

X-Ray Spectra from Soot Particles and System Background (100 Second Analyses)

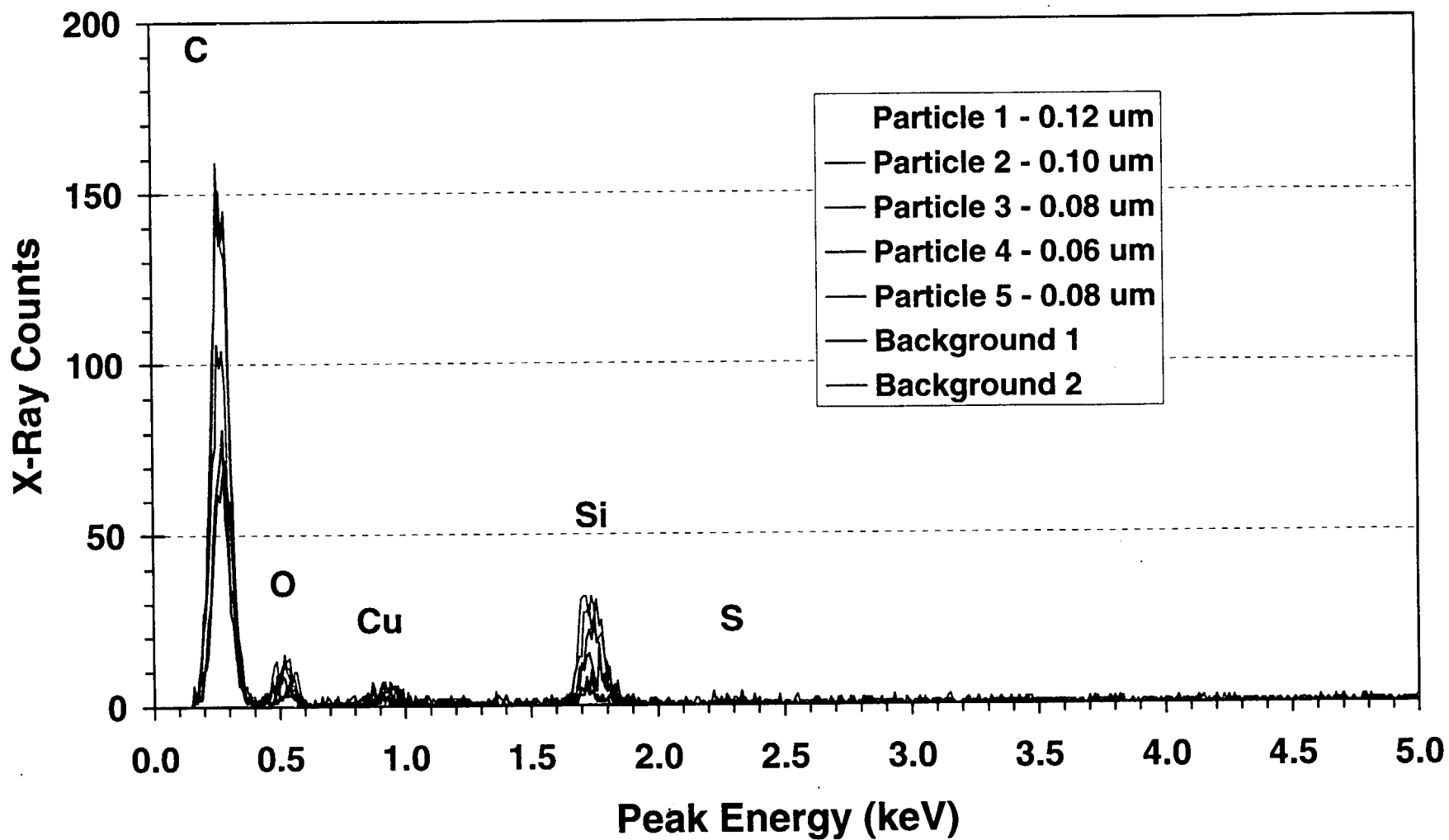


Figure 4

coating on a very small particle might not be detectable whereas a similar coating on a larger particle probably would. The several F-16 exhaust samples where High-S fuel was burned showed higher numbers of C-O-Si particles that contained detectable S (in the 25-75% range) and larger number fractions of "C-O-Si, with S" particles than did similar samples from JP-8-powered F-16's.

Exhaust samples were collected at various distances behind the F-16 aircraft with the hope of being able to determine if there were characteristic differences in the particles related to plume age. In general, the morphology and elemental composition of soot particles collected at all separation distances were similar. The maximum distance sampled behind the aircraft was ~1 nautical mile, and samples taken at this distance always contained at least some aerosols from the closer distances. Figures 5 and 6 show particles from an F-16 exhaust sample (JP-8 fuel) collected at 0.05 nautical miles separation at 10.7 km altitude. Most of the soot particles present appeared to be of the chain aggregate morphology, although a few are visible as small spherules. These could either have impacted as observed or have fragmented off the aggregates. The classic chain aggregate soot morphology was observed regardless of which type of fuel the F-16 used (JP-8, High-S, and Low-S). Most soot particles contained no detectable S, and H₂SO₄ droplets were not observed in significant numbers. Figures 7 and 8 show particles collected behind an F-16 (High-S fuel) at 0.1 nautical mile separation. At separation distances of 0.1 nautical miles and greater, H₂SO₄ droplets were usually observed in significant numbers in the High-S fuel samples. The soot morphology is clearly that of chain aggregate soot, although perhaps not as nicely formed as the morphologies observed at closer separation distances. Both figures clearly show the presence of H₂SO₄ droplets, which are easily recognized by their characteristic acidic sulfate satellite ring morphology. These H₂SO₄ droplets have spread out over the film surface upon impaction to several times their original (atmospheric) diameters, and the analyzed "particles" are residual material left after water loss in the vacuum. These aerosols appear to be primarily external mixtures of the sulfate and soot, with most H₂SO₄ droplets showing no association with soot particles, and vice versa. X-ray analysis of discrete soot particles showed most contained little to no detectable S. Again, it must be stressed that detection of S in or on these soot particles is dependent on the absolute mass of S present, so thin coatings on small (< ~0.1 μm) particles are likely to be undetectable. Thus, the presence of S on small soot particles can not be ruled out.

Sulfuric acid droplets were observed in all samples, but usually in number fractions far lower than the soot. The appearance of H₂SO₄ droplets in some of these samples could be from nucleation of S-containing vapors in the exhaust or from mixing and coagulation of ambient (non-plume) H₂SO₄ droplets from the atmosphere. Observation of H₂SO₄ droplets has a practical lower size limit of ~0.03 μm diameter; if the particles are smaller than this the contrast with the thin film is insufficient to permit detection. We can not dismiss the possibility that large numbers of sub-0.3 μm sulfate particles were collected and not observed in the impactor samples.

Exhaust particles from the C-130 aircraft (which always burned JP-5 fuel) usually appeared as soot aggregates, often seeming to have a coating or to be associated with a viscous or semi-solid phase in aggregates. The coating on individual particles was usually visible as a residue or spot around the particle, suggesting that the liquid or viscous material at least partially transferred to the formvar film after impaction. Often particles were formed into aggregate masses that resembled amorphous blobs, which lost most or all of the chain aggregate

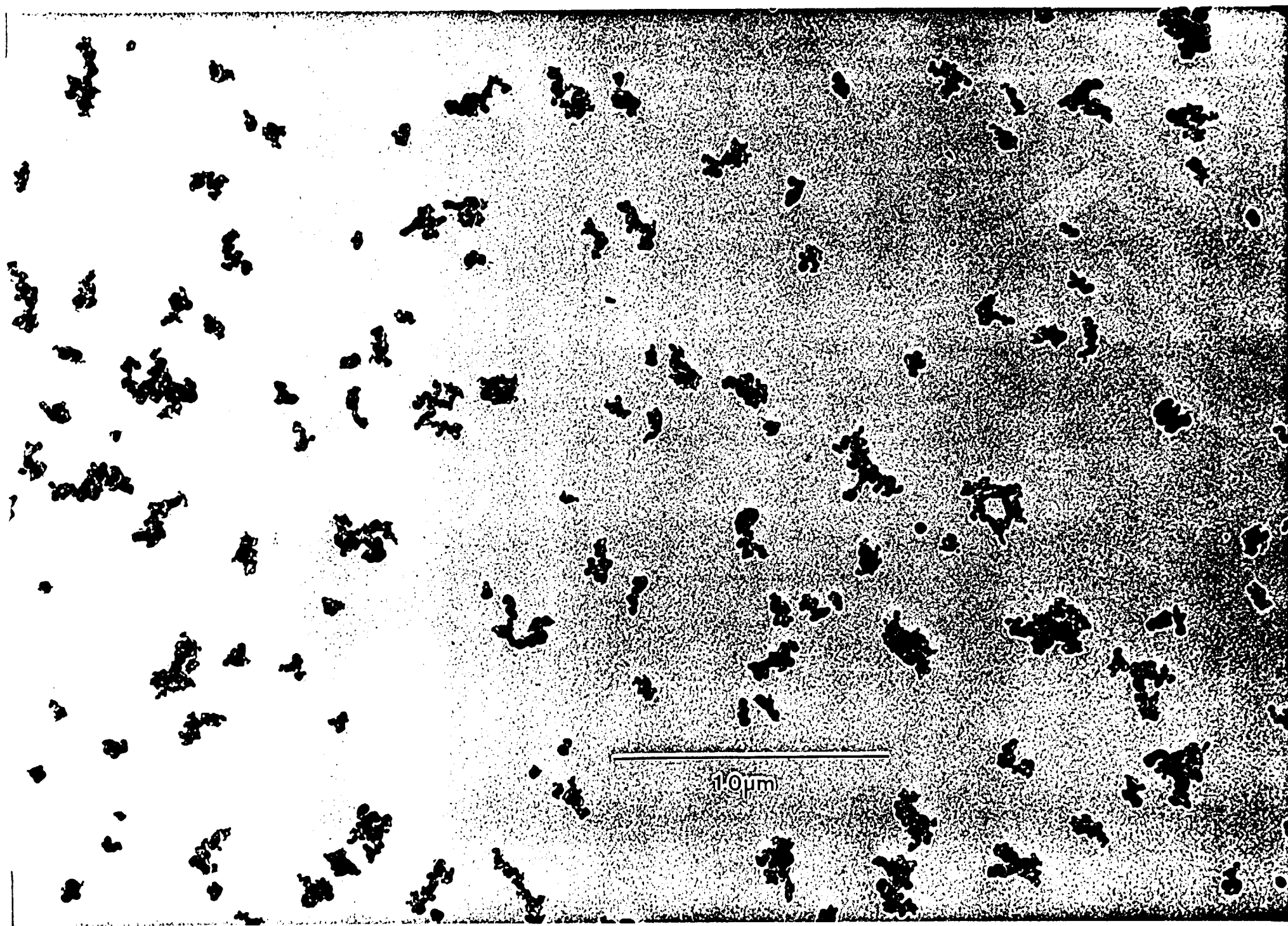


Figure 5

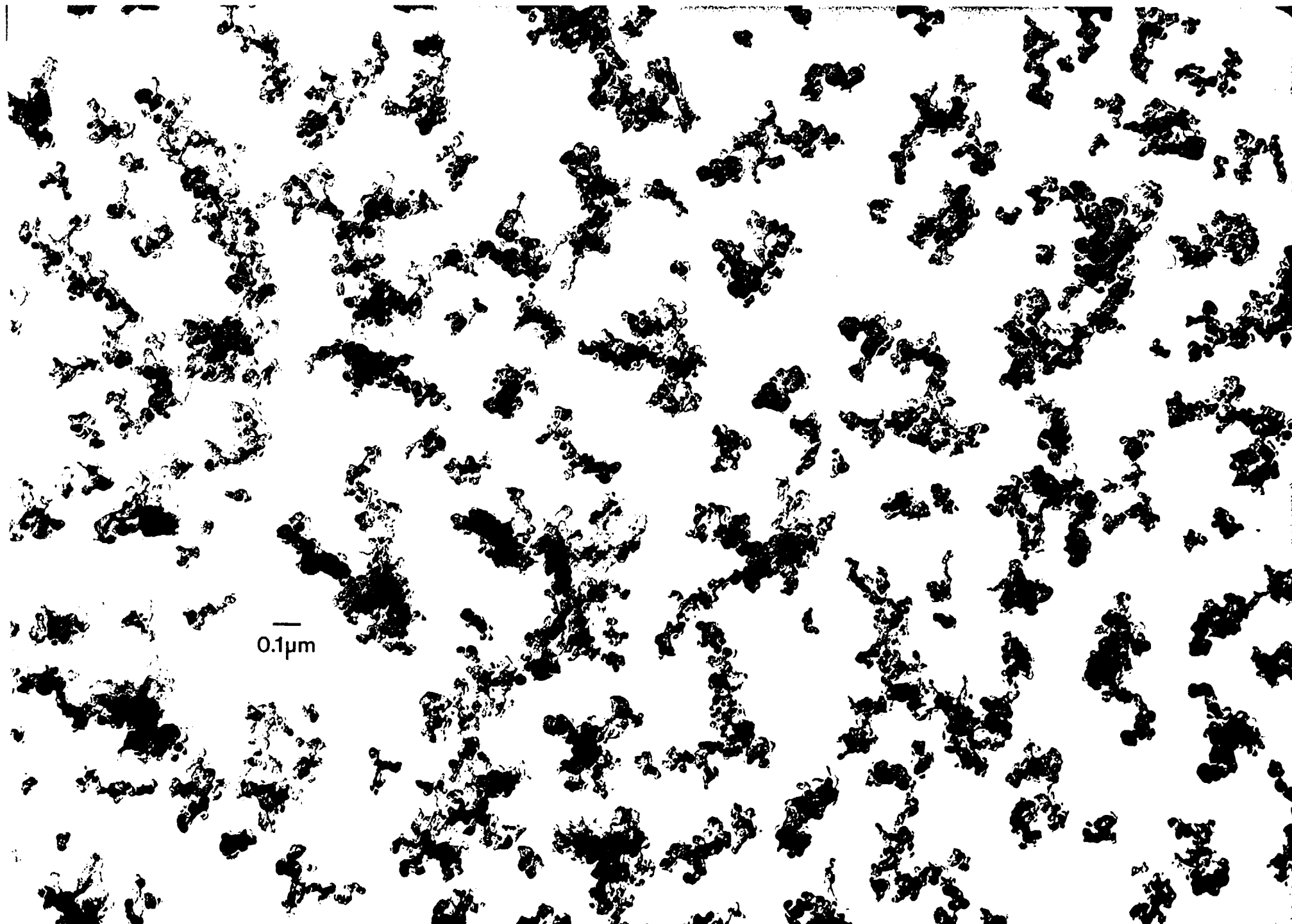


Figure 6

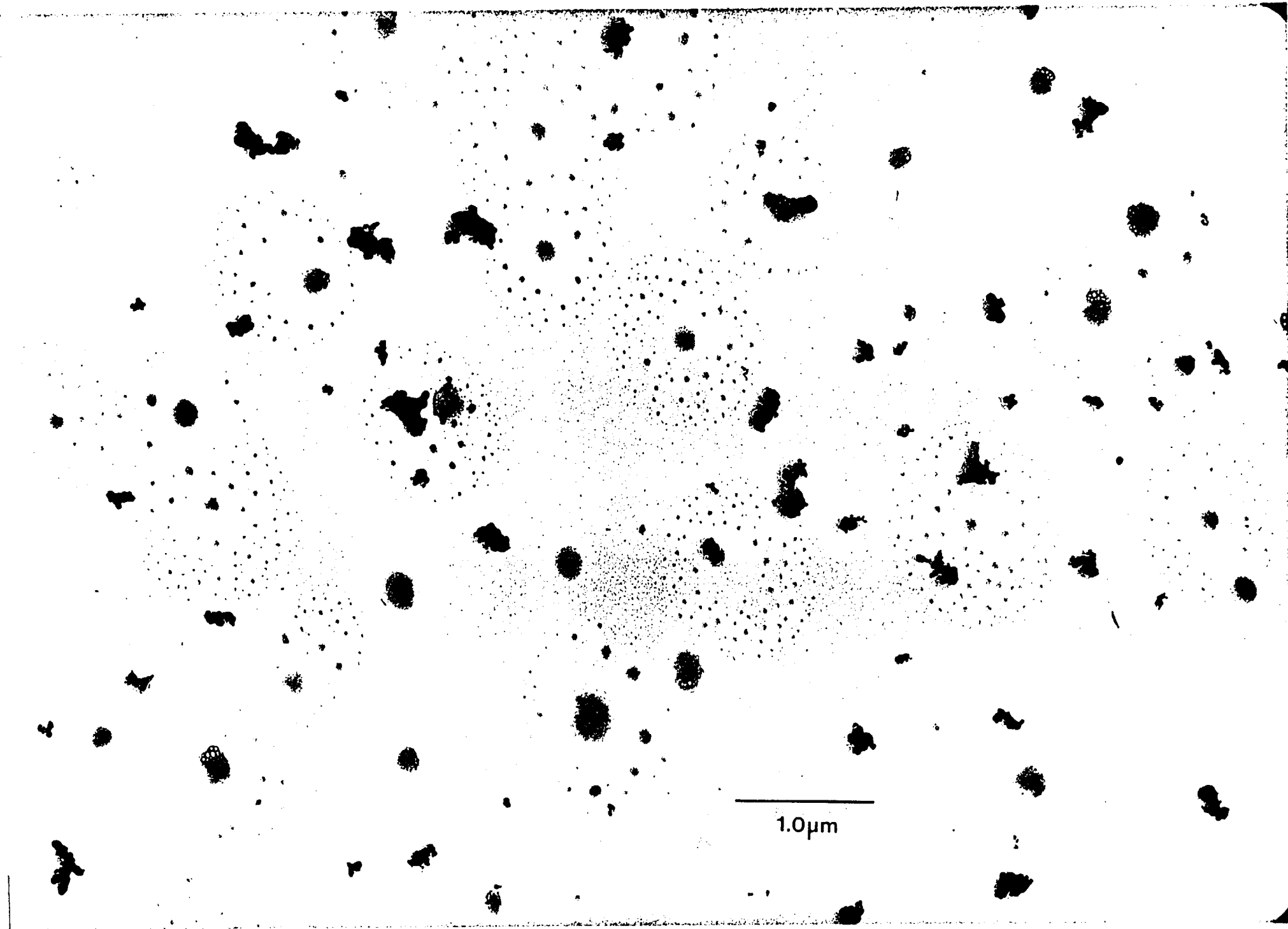


Figure 7

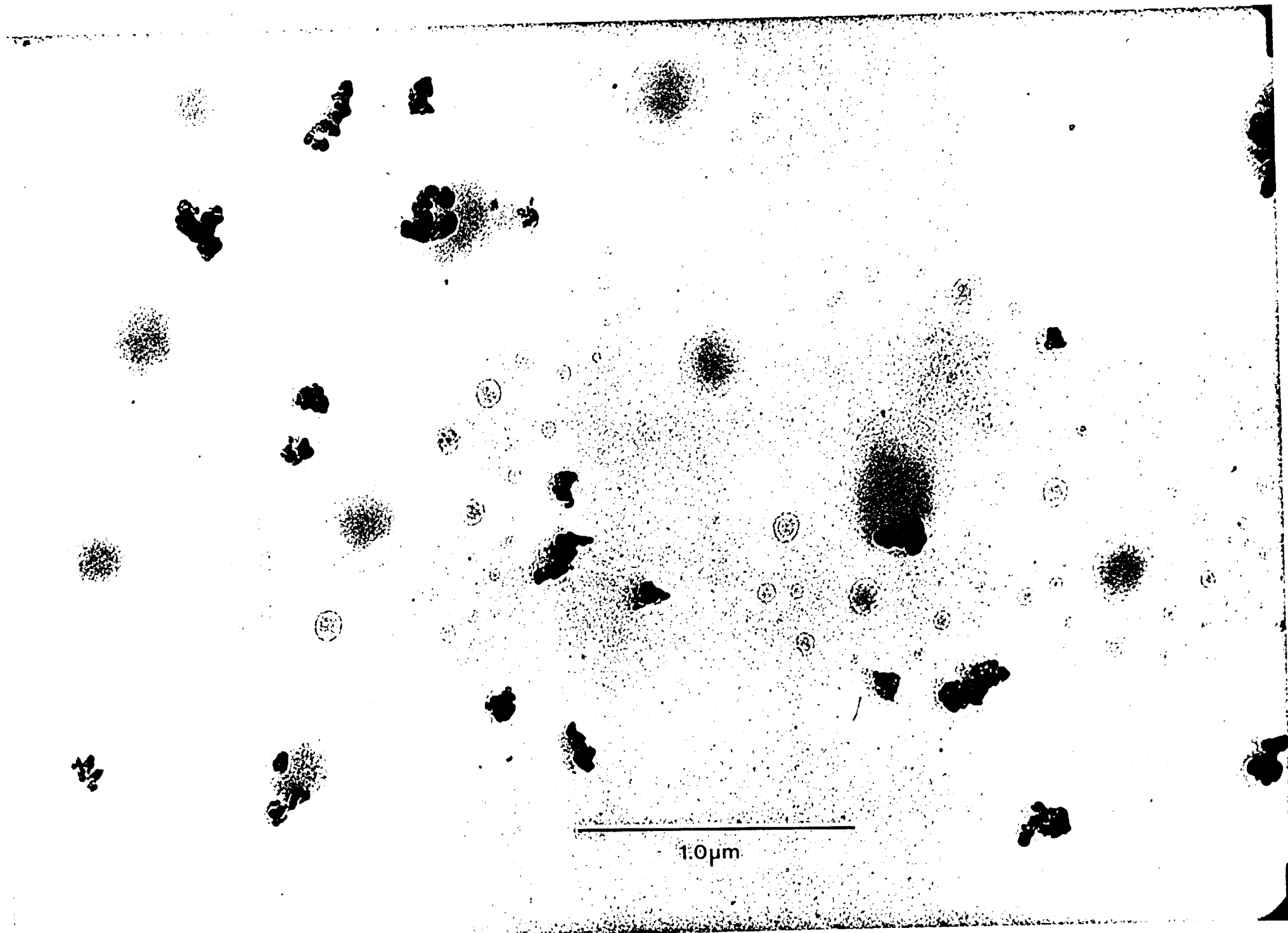


Figure 8

characteristics of the soot particles. Organic vapors in the exhaust plume may have condensed onto soot particles after plume aging resulted in a low enough temperature for condensation to occur. We speculate that these coatings were responsible for our observation that it was quite difficult to obtain sharp clear images of C-130 exhaust particles. Figure 9 shows individual particles from a C-130 sample (~50-m separation) that exhibit the chain aggregate soot with residue and blob morphologies. Chemically, the elemental composition of these particles is indistinguishable from those collected from the F-16 aircraft (Figure 5).

All analyzed samples of C-130 aircraft exhaust exhibited the aggregate soot with residue morphology, whereas only the F-16 samples collected at the largest separation distances did, and these samples typically showed smaller residue spots suggesting a smaller organic component. Well-formed soot chain aggregates without residues of the type observed in Figure 5 were not observed in any of the C-130 samples.

Since the C-130 always burned JP-5 fuel, the effect of fuel type on soot characteristics could not be determined. Samples were collected over distances ranging from about 100 ft. to approximately 1 nautical mile behind the source aircraft. The two C-130 samples collected at the largest separation distances (970619, Sample 21, 0.5 nautical miles separation and 970619, Sample 20, 1 nautical mile separation) showed the highest number fraction of sulfate particles of any samples. These two samples contained sulfate (S-O) and sulfate with salts (S-O, with Na, K, and/or Cl) in number fractions approaching or exceeding 50%. Other C-130 exhaust samples, even ones collected at following distances near 0.5 nautical miles, did not exhibit these high fractions of sulfate particles.

V. Characterization of Individual Samples

This section describes the 500-particle counting and analysis process for each of the SNIF III samples. Figure 10 shows the sampling parameters for each SNIF III sample.

Flight 6/11/97 Sample #1 – C-130 Aircraft – JP-5 fuel – 0.5 Nautical Mile Separation

The central aerosol deposit was found during a re-analysis of this grid. It is well off center and was completely missed during the initial look at this grid. The loading on this grid is fairly light – it could easily be a factor of 2-3 heavier and be better for analysis. The most frequently observed particles in this sample are small amorphous blobs (it is difficult to describe these in any other way). These particles usually have a rounded shape, are of light contrast with the collection film, and tend to average a few tenths of a micrometer in diameter over the entire grid. They do not appear by morphology to be classic chain aggregate soot particles, although there are some of these that resemble chain aggregates. The possibility exists that these could be soot particles coated with something else. The composition of these particles are mostly C (60-90% by mass), with some O and Si in smaller amounts. Oxygen is usually present in mass fractions of a few percent, and Si typically at a similar level, although Si is occasionally present in larger amounts (up to 20% by mass). Trace elements are occasionally observed in these particles. The rounded shapes of these C-O-Si particles suggest that they may have impacted as liquid, dual-phase or moist solid particles. Are these particles soot? Could they be rich in organic C, either as primary emitted particles or formed from condensable vapors in the exhaust? This class of



Figure 9

SNIF-III Flight	flight date	Source Aircraft	AC Fuel	Separation N miles	grid sample	hr mn sc	seconds exposed	flight alt (km)	Average dCO2	Average dUPC_T	Average dUPC_H	Average dCNC_T	Average dCNC_H	Comments
sn08	970611	C-130	JP-5	0.5	1	18 15 5	135	3.2	23.7	716077	103316	44322	20817	#4 engine
sn08	970611	C-130	JP-5	0.5	2	18 18 54	149	3.2	28.6	148380	140233	54268	25838	#2 engine
sn08	970611	F-16	JP-8	0.5	3	18 22 43	71	3.2	51.5	302747	272332	104146	50306	#2 engine
sn10	970613	F-16	JP-8	0.3	1	16 16 28	71	9.0	15.3	56949	36921	15168	8331	83% power
sn10	970613	F-16	JP-8	0.3	2	16 23 33	93	8.8	50.2	118883	103397	48511	20483	90% power
sn10	970613	F-16	JP-8	0.3	3	16 53 33	74	11.8	4.7	456084	47749	8241	33313	in climb
sn10	970613	F-16	JP-8	0.2	4	16 56 40	60	11.8						84% power
sn10	970613	F-16	JP-8	0.7	5	16 59 37	88	11.9	11.2	79450	34498	13152	7620	Contrails
sn12	970619	C-130	JP-5	0.1	23	14 19 46	201	2.5	75.0	413896	350716	133733	69795	
sn12	970619	C-130	JP-5	0.03	22	14 26 33	301	5.2	196.8	1025723	777643	287112	125939	
sn12	970619	C-130	JP-5	0.5	21	14 33 4	301	6.7	45.2	756367	178613	74201	32893	
sn12	970619	C-130	JP-5	1	20	14 41 59	501	6.7	13.7	410089	58533	25605	12450	
sn12	970619	Bkgnd	-		19	15 21 2	401	6.5	1.1	4931	5076	1683	994	
sn14	970625	F-16	Hi S	0.1	18	14 40 19	60	9.3	84.4	2901616	157686	80052	49038	80-90% power
sn14	970625	F-16	JP-8	.1 to 1	17	14 50 0	100	9.3	245.7	399082	406084	186353	105569	80-90% power
sn15	970625	F-16	Hi S	0.2	16	18 45 6	404	10.8	31.3	1439145	67867	33018	24864	80% power
sn15	970625	F-16	Hi S	0.1	15	18 55 15	251	10.8	71.9	2250158	166581	81684	65280	85% power
sn15	970625	F-16	JP-8	0.05	14	19 10 7	254	10.7	161.7	441175	384870	189346	131688	80% power
sn15	970625	F-16	Hi S	.1 to 1	13	19 26 50	530	11.4	40.4	1797277	103110	50535	41607	Contrail
sn19	970627	F-16	Lo S	0.1	19	14 6 21	134	10.7	58.1	181935	156476	75466	70555	Contrail
sn19	970627	F-16	JP-8	0.1	18	14 29 43	62	10.6	76.6	197734	202458	94533	96568	Contrail
sn19	970627	Bkgnd	-		17	14 50 12	101	10.4	1.5	16801	8550	7456	1158	
sn20	970627	F-16	Lo S	0.1	16	18 10 56	284	9.1	112.8	268771	226378	123854	71263	80-90% power
sn20	970627	F-16	JP-8	0.1	15	18 38 28	139	9.1	89.6	212337	174446	103331	60224	90% power
sn20	970627	Bkgnd	-		14	18 47 41	101	8.0	12.5	5446	5426	1365	539	
sn20	970627	Bkgnd	-		13	18 53 55	621	7.4	5.4	1804	1807	387	181	

Figure 10

particle was observed in many other samples, and these particles are referred to as "blob", "amorphous blob", or "condensation blob" particles.

Two other particle classes were observed in large numbers on this grid. Particles in one of these classes (Low Counts) resembled the C-O-Si particles morphologically but did not give an x-ray spectrum significantly above system background. Most of these Low Counts particles were pretty small (~0.07 μm diameter or smaller), and this size is approaching that where chemical information cannot be routinely obtained. Thus, many of these Low Counts particles may well have been of the C-O-Si type, but were just too small to get the chemical information required for classification. Sulfate particles (usually showing the acidic sulfate morphology) were also present in relatively low concentrations (<10% by number).

Results of the 500-particle classification:

C-O-Si blob particles	358
Low Counts particles	90
Sulfate particles	43
Si-rich	5
C-O particles	4

Flight 6/11/97 Sample #2 – C-130 Aircraft - JP-5 fuel – 0.5 Nautical Mile Separation

Resembles Sample #1 from this date, although particle loadings are even lower (several times lower) than in that sample. Many squares show only a few particles. Major particle types are the same, with a few other types of particles present. The C-O-Si particles typically resemble small blobs but many are also present that appear as aggregates. A viscous coating appears to be present and may smooth out the fine morphological features in these aggregates. Some larger particles are present (0.3-0.5 μm diameter), showing the same morphology and composition as the smaller ones. Could this suggest particle bounce from the pre-collection surface (first observation of this)?

Results of the 500-particle classification:

C-O-Si blob particles	382
Low Counts particles	70
Sulfate particles	39
Si-rich	3
Na-Cl	3
Crustal	2
Al-rich	1

Flight 6/11/97 Sample #3 – C-130 Aircraft - JP-5 fuel – 0.5 Nautical Mile Separation

Resembles previous two samples from this flight. C-O-Si particles are of the same general composition and morphology as before, but the loadings in this sample are better. There are far more particles on this grid than on the Sample #2 grid, and slightly more than on the Sample #1 grid. More sub-0.1 μm particles are visible in this sample, but the composition does not seem to change significantly. There are more particles with Si near 20% mass fraction – usually it's lower than this. The C-O-Si particles that had slightly higher Si mass fractions were still classified as C-O-Si blobs. Classic chain aggregate soot particles were still not observed in this sample. Blob particles may be coated soot – some appear to have a grossly chain aggregate shape. Higher-Si particles without much C were classified as Si-rich. A small fraction of the C-O-Si particles also show minor (more than trace) amounts Na and sometimes S and Cl. These other constituents were not observed in higher than trace amounts in the previous samples from this flight. For the first time, one very heavily loaded grid square was observed in a low loading area. Figure 11 shows an example of this inhomogeneous deposition phenomenon. Grid squares adjacent to this square show very few particles. Is this the first case of ablation from the pre-collection substrate? Particles analyzed in this square (not included in the 500-particle classification) show higher Si than usual, often ~20% mass fractions, both from individual particle and bulk material analyses. Could a large Si-rich blob either have bounced off or been ejected from the pre-collection substrate? Could some of the higher-Si particles in other squares be there because of this possibility?

Results of the 500-particle classification:

C-O-Si blob particles	380
C-O-Si, with Na	21
C-O-Si, with S	4
C-O-Si, with Na, S	5
C-O-Si, with Na, Cl	1
C-O-Si, with Na, S, Cl	3
C-O particles	1
Low Counts particles	34
Sulfate particles	19
Si-rich	19
Na-Cl	3
Na-Cl-S	5
Na-S-O	4
Crustal	1

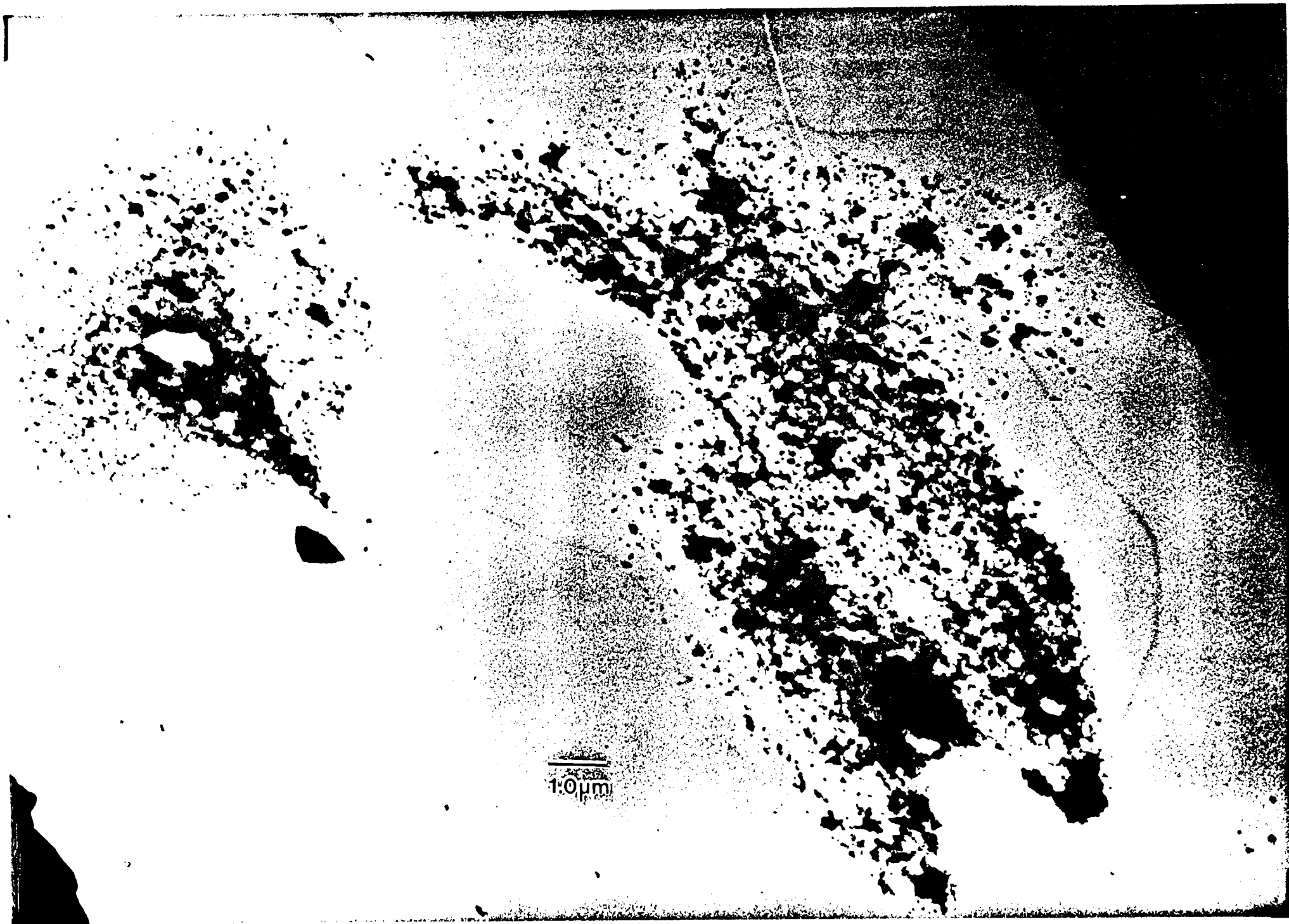


Figure 11

Flight 6/13/97 Sample #1 – F-16 Aircraft – JP-8 fuel – 0.3 Nautical Mile Separation

Particles appear more solid, well formed, and of higher viewable contrast with the thin film than the amorphous or “blob” particles in the 970611 samples. Solid particles with high C content could be soot, although chain aggregate morphology is not evident in most of the particles. The distinction between C-O-Si solid rounded particles and chain aggregate particles may be too fine. The small solid rounded particles appear to have the same contrast with the thin film and elementally are indistinguishable with the branched soot particles. Both particle types appear to be aircraft soot. Also, “rounded” does not mean “round” - often small lobes are visible. A rounded particle really just has “soft” rather than sharp edges and is roughly equidimensional. It is possible that many of the solid rounded particles were at one time associated with chain aggregate soot particles, and they may have broken off upon entering the impactor. The distinction was made only to give some idea of the relative number of branched versus rounded particles on the analysis substrate. The typical, or at least the most commonly observed, particle is a sub-0.1 μm diameter, rounded, solid particle of medium viewing contrast with the film substrate and with little or no branching structure. Particles substantially larger than the nominal $\sim 0.2 \mu\text{m}$ aerodynamic diameter upper size limit (imposed by the pre-collection substrate) are observed; these are usually in the 0.3-0.5 μm range and are infrequently observed (perhaps one particle in one hundred). In most cases, the composition of the larger particles is very close to the composition of the numerous sub-0.1 μm particles, that typically being major C with a few percent O and Si. In this sample, no trace elements (including S) were observed in the C-O-Si particles. As in the 970611 samples, some particles showed higher Si/C ratios; if C was not also a major component these particles were classified as Si-rich.

Results of the 500-particle classification:

C-O-Si solid rounded particles	287
C-O-Si blob particles	15
C-O-Si chain aggregates	131
C-O particles	5
Low Counts particles	18
Sulfate particles	16
Si-rich	28

Flight 6/13/97 Sample #2 – F-16 Aircraft - JP-8 fuel – 0.3 Nautical Mile Separation

This grid was mishandled such that it was folded over on itself. The grid was straightened and flattened to the extent possible and put into the holder. Numerous broken grid squares are observed – this combined with the lower available viewable area of this smaller-mesh grid make this grid an example of why the 200-mesh size is preferred. It was difficult to locate 500 particles in different regions of the grid for classification on the few intact grid squares. Fortunately, the CAD region was mostly intact and lots of particles from there could be analyzed. There were, however, a few squares that showed high numbers of particles well away

from the CAD. Looks like the same deposition problem as before.

The particles on this grid appear to have impacted as wet or blob particles, with fewer dry, chain aggregate soot particles observed. The particles do not show sharply defined edges, suggesting that they are moist blobs or are encased in a viscous or goeey material. Could this sample be compromised because of ablation of the moist deposit on the pre-collection substrate? Metallic particles are also observed in this sample. They are quite easy to spot because they are extremely electron-opaque, and appear quite dark in the transmission mode. X-ray spectra of most of the smaller individual particles showed the C-O-Si signature that has come to be expected. Bulk analyses of the larger, multiple-particle masses in the CAD and in the high-loading "islands" also showed C-O-Si, but usually with higher Si (sometimes in amounts nearly as large as the C). Trace elements were often observed in spectra from the large particulate masses.

Results of the 500-particle classification:

C-O-Si solid rounded particles	136
C-O-Si blob particles	244
C-O-Si chain aggregates	33
Low Counts particles	25
Sulfate particles	7
Si-rich	47
Ti-rich	3
Cr-rich	2
Cr-Fe (Cr > Fe, not stainless steel)	1
Al-S-Cl	1
Mixed salts (Na-Mg-S-Cl-K)	1

Flight 6/13/97 Sample #3 – F-16 Aircraft - JP-8 fuel – 0.3 Nautical Mile Separation

Most of the particles on this grid have the C-O-Si composition and some of these (perhaps 5%) also show a little Na and/or S. Most of the C-O-Si particles containing Na and/or S were smaller than 0.1 μm . The larger C-O-Si particles rarely showed any trace elements in this sample. A few particles were composed of just C and O with no Si above background. As in other samples, C-O-Si particles appear to show more than one consistent morphology; these are the amorphous "blobs" and the small solid particles. The blobs again appear to be wet, moist or dual-phase in nature. Often, it is difficult to distinguish the "blob" particles from the solid-looking ones, since they are often both about the same size and rounded. There seems to be a continuous gradation from blob to solid, covering various degrees of solidity. This is a subjective distinction that may not be valid to make. These particles may in fact all be of the same morphology; they definitely are of very similar composition. For now we will make the distinction between solid-appearing and moist-looking (blob) C-O-Si particles, with the caveat

that we may have to combine the numbers from the two groups into one class. This applies to all the other samples from this study also. The only morphological distinction that we can be absolutely sure of is the distinction of chain aggregate soot vs. non-aggregates.

Particles substantially larger than expected are again observed in low numbers. These larger particles are in the 0.3-0.8 μm range, and again show roughly the same composition as the smaller ones.

Results of the 500-particle classification:

C-O-Si solid rounded particles	64
C-O-Si blob particles	300
C-O-Si chain aggregates	12
C-O-Si, with Na	16
C-O-Si, with S	8
C-O-Si, with Na, S	10
C-O-Si, with Na, S, Cl	1
C-O particles	6
C-rich	6
Low Counts particles	29
Sulfate particles	11
Si-rich	36
Ti-rich	1

Flight 6/13/97 Sample #4 – F-16 Aircraft - JP-8 fuel – 0.2 Nautical Mile Separation

This was another poorly handled grid. Grid was straightened and flattened and then inserted in microscope for analysis. This is another small-mesh grid. This sample very closely resembles Sample #3 from this date, with the vast majority of particles being of the C-O-Si composition and occasionally showing trace Na and S. Again, smaller (sub-0.1 μm) particles are more likely to show Na and S, although some particles of this composition are >0.2 μm diameter. The presence of Na and S does not appear to influence the physical phase (blob vs. solid) of the particle. Both types showed these trace or minor elements. Not as many larger (>0.3 μm) particles as in Sample #3, perhaps a few particles per thousand.

Results of the 500-particle classification:

C-O-Si solid rounded particles	111
C-O-Si blob particles	262
C-O-Si chain aggregates	4

C-O-Si, with Na	23
C-O-Si, with S	2
C-O-Si, with Na, S	15
C-O-Si, with Na, S, Cl	5
C-O particles	7
C-rich	2
Na-S-O	12
Low Counts particles	38
Sulfate particles	7
Si-rich	9
Ti-rich	1
Crustal	2

Flight 6/13/97 Sample #5 – F-16 Aircraft - JP-8 fuel – 0.7 Nautical Mile Separation

Mostly small ($<0.2\ \mu\text{m}$) solid C-O-Si particles on this grid, with some of the lighter “blob” particles of the same composition. A small but significant fraction of the C-O-Si particles (more than on the last few grids) show the soot chain aggregate morphology. Some agglomerate particles are very large ($>1\ \mu\text{m}$ across). Not many of these particles show the Na, S, or Na/S trace element signature that was prevalent in the previous few grids. A few metallic particles were also observed.

Results of the 500-particle classification:

C-O-Si solid rounded particles	263
C-O-Si blob particles	92
C-O-Si chain aggregates	59
C-O-Si, with Na	3
C-O-Si, with S	1
C-O particles	5
C-rich	1
Na-S-O	1
Low Counts particles	27
Sulfate particles	29
Si-rich	16
Crustal	1

Fe-rich	1
Al-rich	1

Flight 6/19/97 Sample #23 – C-130 Aircraft – JP-5 fuel – 0.1 Nautical Mile Separation

CAD region covered with what appears to be a solidified (based on the cracking), originally liquid deposit of the C-O-Si composition. Other particles are visible in this deposit, usually because they contain other elements (e.g., Ti) that appear darker in the electron beam. Figure 12 shows a photomicrograph taken at 20,000X that illustrates this problem. Could this be a vapor condensation or liquid collection problem?

Away from the CAD is where individual particle analysis occurred. Most discrete particles in this sample are C-O-Si particles of the “condensation blob” type; a few contain darker inclusions. C-O-Si particles do not show trace Na in this sample. There seem to be more Ti-rich particles in this sample than in previous samples. Mean analyzed particle size is ~0.1 μm , although a lot of particles are much smaller.

The vast majority of the solid mass of this sample is in the CAD and not visible (or analyzable) as individual particles. But the bulk aerosol composition is similar to that of most of the discrete “blob” particles. We have to ask whether these observations suggest that this sample was compromised in some way. The next sample from this day (#22) was apparently collected in a similar location behind the aircraft and shows some different soot particle morphologies and a lesser filmy deposit. Could this be a different portion of the exhaust plume?

Results of the 500-particle classification:

C-O-Si blob particles	396
C-O-Si solid rounded particles	32
C-O-Si chain aggregates	4
C-O-Si, with S	6
C-O particles	9
C-rich	2
C-rich, with trace Cr, Fe, K	1
Na-S-O	1
Low Counts particles	17
Sulfate particles	12
Si-rich	9
Si-rich, with Al	1
Crustal	1
Ti-rich	8



Figure 12

Flight 6/19/97 Sample #22 – C-130 Aircraft – JP-5 fuel – 0.03 Nautical Mile Separation

Heavy particulate loading in the CAD region. Composition of the heavy CAD deposit is C-O-Si, with higher than expected Si (perhaps 30% by mass in some areas, 10-20% in most others). The larger agglomerate particles usually show a higher mass fraction of Si than do the individual chain aggregate particles. Unlike the previous sample (#23) from this flight, discrete soot-like particles were observed over much of the grid surface. Particles on this grid were overwhelmingly of the usual C-O-Si composition and the chain aggregate morphology. Most particles (including the aggregates) were smaller than 0.2 μm . Focusing the image was difficult for this sample because both the formvar film and the particles appeared to have some sort of film or coating (similar to that on the last sample but not as heavy) on them. This coating was especially apparent when attempting to obtain sharp, medium-magnification (20,000x) images of the grid bars and particles, which almost always are easily obtainable and were not in this case. In this sample, particles appeared blurry and would not come into sharper focus. Figure 9 illustrates this problem. Particles in this FOV clearly show the chain aggregate soot morphology and C-O-Si composition. A dark spot is visible around most of the particles that could indicate the deposition or seepage of liquid-phase material from the aggregates to the film surface. The darker spots show no obvious elemental signature (like S, for example) in excess of the C-O-Si spectrum from the particle. The spots could be composed of organic material that shows C and a little O, and they would be indistinguishable from the particle spectra.

Results of the 500-particle classification:

C-O-Si chain aggregates	329
C-O-Si solid rounded particles	62
C-O-Si blob particles	12
C-O-Si, with S	15
C-O particles	3
Low Counts particles	12
Sulfate particles	45
Si-rich	22

Flight 6/19/97 Sample #21 – C-130 Aircraft – JP-5 fuel - 0.5 Nautical Mile Separation

Overall, there was a pretty light loading of particles on this grid. The CAD region was never located because the grid was mishandled and tape was sticking to much of the underside. This eliminated ~25% of the grid from analysis. A nicely dispersed deposit of particles was present for analysis on the remaining grid surface. Both C-O-Si and S-rich particles are present on this grid in similar numbers. Analyzed S-rich (sulfate) particles typically appear <0.1 μm in diameter

and lose mass (volatilize) under a condensed electron beam. Over half of the S-rich particles also contain Na, K, and/or Cl as minor or trace elements. These particles usually did not show an acidic sulfate morphology (satellite rings of smaller particles); this suggests that many were at least partially neutralized upon collection. Again, these sulfate particles were probably significantly smaller than 0.1 μm in the atmosphere. The C-O-Si particles are present as both solid particles and amorphous blobs, and generally do not appear as chain aggregates, although these are present in smaller numbers. The soot often looks to be compacted, and sometimes appears as rounded solid particles in the 0.05-0.20 μm size range.

Results of the 500-particle classification:

C-O-Si solid rounded particles	115
C-O-Si blob particles	45
C-O-Si chain aggregates	22
C-O-Si, with S	3
Low Counts particles	12
Sulfate particles (S-O)	139
Sulfate with Na, K, and/or Cl	162
Si-rich	2

Flight 6/19/97 Sample #20 – C-130 Aircraft – JP-5 fuel - 1 Mile Separation

This grid did not show a well-defined CAD region, and had particles inhomogeneously distributed over the grid surface in small high-loading islands. Particles on this grid were of two main types – C-O-Si particles and particles showing all or most of the elements Na, Cl, K, and S. Both Na and S were usually present in this later class of particles, with K frequently and Cl less frequently observed. Carbon is not present in a major mass fraction in these particles, although small C peaks are often visible. These salt-like particles are unstable (volatile) in the condensed electron beam and are often much larger (up to several micrometers in size) than expected given the pre-collection surface upstream of the grid. The uneven deposition pattern on the formvar film suggests that this sample might have experienced pre-collection substrate ablation and particle bounce in the impactor. The C-O-Si particles were more often spread out nicely and were usually smaller than $\sim 0.25 \mu\text{m}$ in diameter, while the Na-S-K-Cl particles were frequently observed as large masses in the deposition islands. Based on the morphology, the deposition patterns, the particle size and the propensity for beam damage, the salt-like particles probably were well-hydrated (moist to wet) when collected. Remember that the 500-particle counts are not performed in these deposition “island” regions.

Results of the 500-particle classification:

C-O-Si blob particles	131
C-O-Si solid rounded particles	93

C-O-Si chain aggregates	2
C-O-Si, with S	31
Low Counts particles	20
Sulfate particles (S-O)	44
Sulfate with Na, K, and/or Cl	179

Flight 6/19/97 Sample #19 – Background Air at 22,000 ft

Nice central aerosol deposit near the periphery of the grid. Lots of sub-0.1 μm particles are visible. Soot particles of the “C-O-Si - chain aggregate” type are everywhere, along with small individual spherules and rounded particles of the “C-O-Si – solid” type. Very few blobs are evident. Sulfate particles are present in numbers similar to the soot particles. Figure 13 shows a typical FOV that illustrates the observed particle types and their relative prevalence. Soot particles often showed a darker spot around them that could be related to a liquid phase on the particle at impaction. These spots were not S-rich, suggesting that these “residue” deposits were not sulfate. In some of the observed sulfate particles, miniscule soot particles were also present, suggesting either soot/acid coagulation or soot acting as an acid condensation nucleus. Figure 14 shows a larger sulfate particle with several small C-O-Si particles or fragments on its surface.

The observation of so many soot particles of obvious aircraft origin in this “background air” sample was surprising. Possible reasons for these observations are reviewed below in the Discussion section.

Results of the 500-particle classification:

C-O-Si chain aggregates	151
C-O-Si solid rounded particles	122
C-O-Si blob particles	11
C-O-Si, with S	33
Low Counts particles	8
Sulfate particles (S-O)	164
Sulfate with Na, K, and/or Cl	11

Flight 6/25/97 Sample #18 – F-16 #1 – High S Fuel – 0.1 Nautical Mile Separation

Very large CAD area was observed covering tens of squares. Lots of fine (0.05-0.10 μm) particles on this grid. This sample had the same problem as was observed in Flight 6/19/97, Samples #22 and #23 (C-130 Aircraft at 100' Separation), namely a film appeared to be present that precluded getting a sharp focus in the micrograph images. Particles are predominantly of the C-O-Si composition, usually with a significant amount of Si (10-20% mass fraction) in them. All three types of C-O-Si particulate morphology were observed in this sample. Little or no S

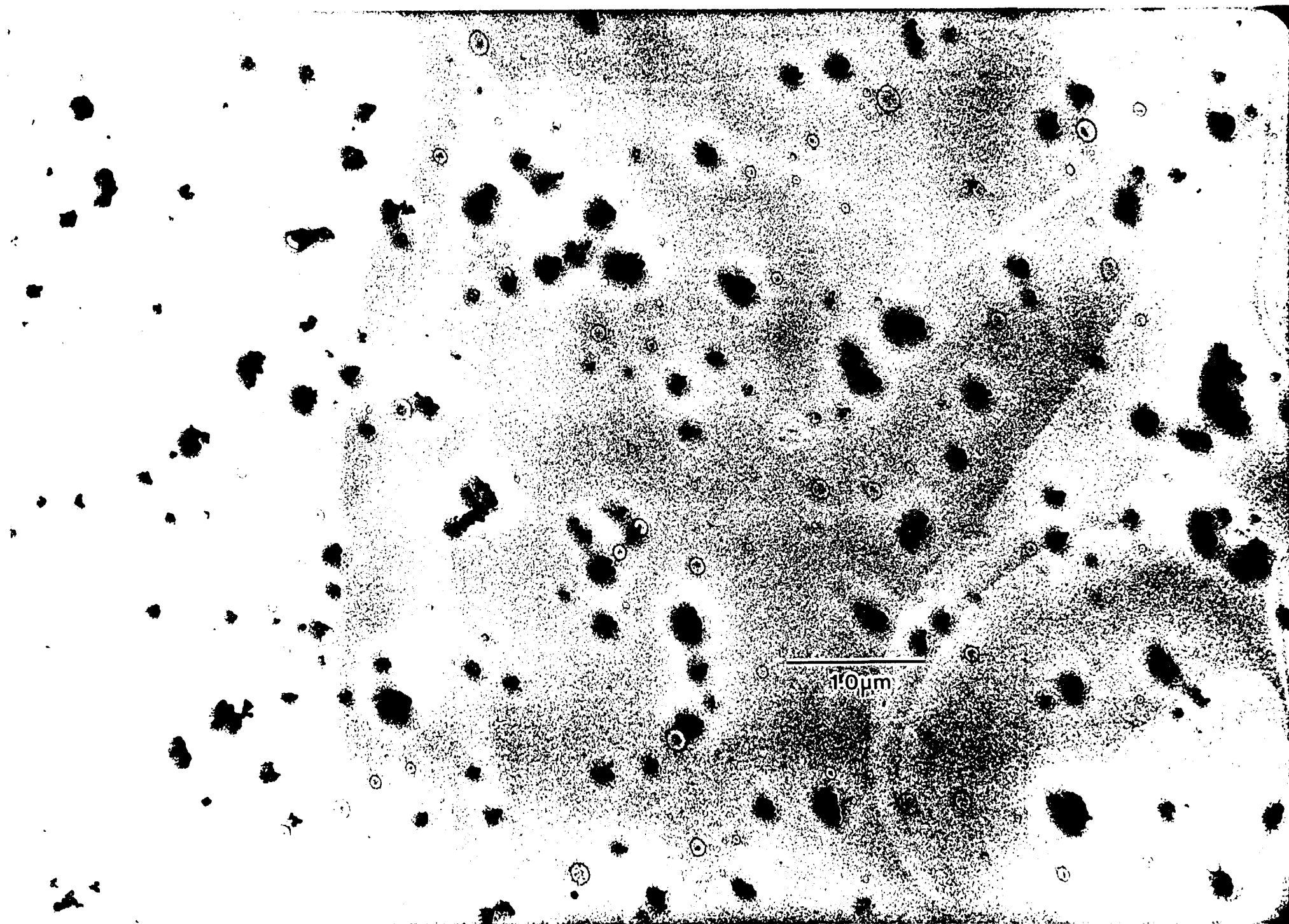
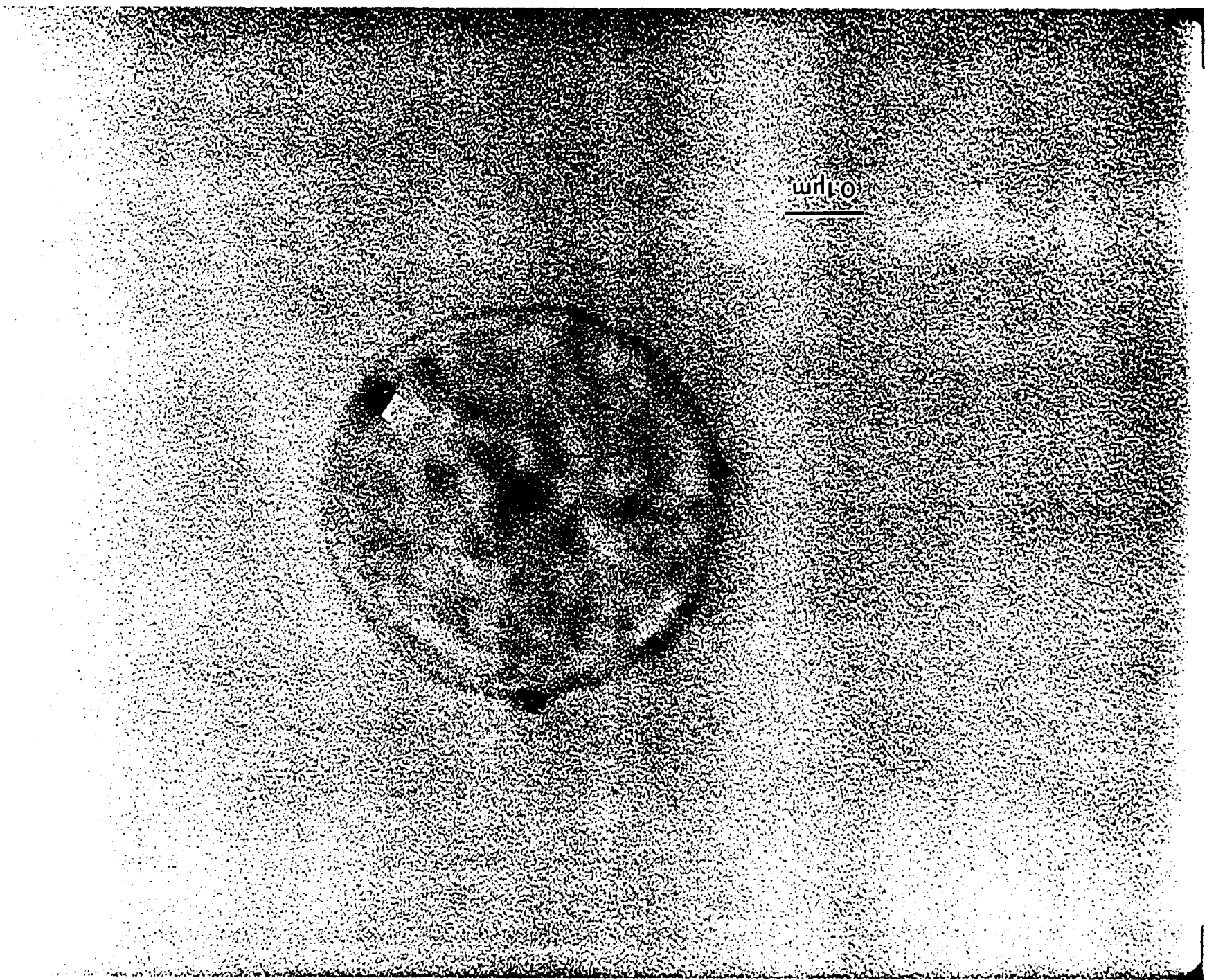


Figure 13



0.1µm

was observed in/on these soot particles, and very few sulfate particles were present.

Results of the 500-particle classification:

C-O-Si blob particles	173
C-O-Si chain aggregates	99
C-O-Si solid rounded particles	142
C-O-Si, with S	13
Low Counts particles	37
Sulfate particles (S-O)	33
Sulfate with Na, K, and/or Cl	2
Ti-rich	1

Flight 6/25/97 Sample #17 – F-16 #2 – JP-8 Fuel – 0.1-1 Nautical Mile Separation

Grid was compressed into a tight ball. Tried to unfold the grid but it started to break. Absolutely no chance for an analysis on this one.

Flight 6/25/97 Sample #16 – F-16 #1 – High S Fuel – 0.2 Nautical Mile Separation

This grid showed a lot of broken-film grid squares, especially in the CAD area. On squares in the CAD where the film was intact, a heavy C-O-Si particulate deposit was present that made it difficult to view and analyze discrete particles. This particulate deposit was comprised mostly of densely packed chain aggregate soot particles, although it was difficult to tell the morphology of C-O-Si particles in the heaviest parts of the deposit. Blob-morphology particles and a filmy coating could have been present in the heavy-deposit areas. The C-O-Si composition was pretty consistent whether analyzing discrete particles or bulk deposits.

Away from the CAD area, individual particles could be analyzed. Sulfate particles were present in this sample, but some of these were pretty large ($>0.3 \mu\text{m}$ diameter). This suggests that they were present in the ambient atmosphere before the aircraft flew by and were not emitted by the aircraft. It is difficult to understand how these larger liquid droplets passed through to impact on this collection surface. Smaller sulfate particles were also observed, but not in large numbers. Lots of C-O-Si particles of all morphologies were present. Many of these particles also showed trace salt components.

Results of the 500-particle classification:

C-O-Si chain aggregates	151
C-O-Si blob particles	106
C-O-Si solid rounded particles	54

C-O-Si, with S	22
C-O-Si, with Na, K, and/or Cl	51
Low Counts particles	37
Sulfate particles (S-O)	63
Sulfate with Na, K, and/or Cl	15
Si-rich	1

Flight 6/25/97 Sample #15 – F-16 #1 – High S Fuel – 0.1 Nautical Mile Separation

Grid was bent and was missing the tab. It was straightened satisfactorily and analyzed. Overall, this sample resembled the last sample closely, with lots of sooty material. Figure 15 shows some of this sooty material in a high-loading area, along with a larger (~0.3 μm) Ti-rich particle. The sooty material was deposited in a CAD region, but also in many deposition islands of the type described above that were distant from the CAD. C-O-Si particles were the dominant composition, with lesser numbers of salt-like and sulfate particles observed. Soot particles were observed to be closely associated with the acidic sulfate droplets (that had spread to larger diameters) in this sample. Figure 7 and Figure 8 are high-magnification photomicrographs from this sample showing the association between soot and sulfate.

Results of the 500-particle classification:

C-O-Si chain aggregates	183
C-O-Si solid rounded particles	115
C-O-Si blob particles	12
C-O-Si, with S	43
C-O-Si, with Na, K, and/or Cl	18
C-O	1
Low Counts particles	11
Sulfate particles (S-O)	84
Sulfate with Na, K, and/or Cl	6
Si-rich	20
Ti-rich	6
Crustal	1

Flight 6/25/97 Sample #14 – F-16 #2 – JP-8 Fuel – 0.05 Nautical Mile Separation

A very well-defined CAD region with a good loading of particles. Particles are mostly chain aggregate soot with very few S-containing particles or C-O-Si particles of the “blob” type

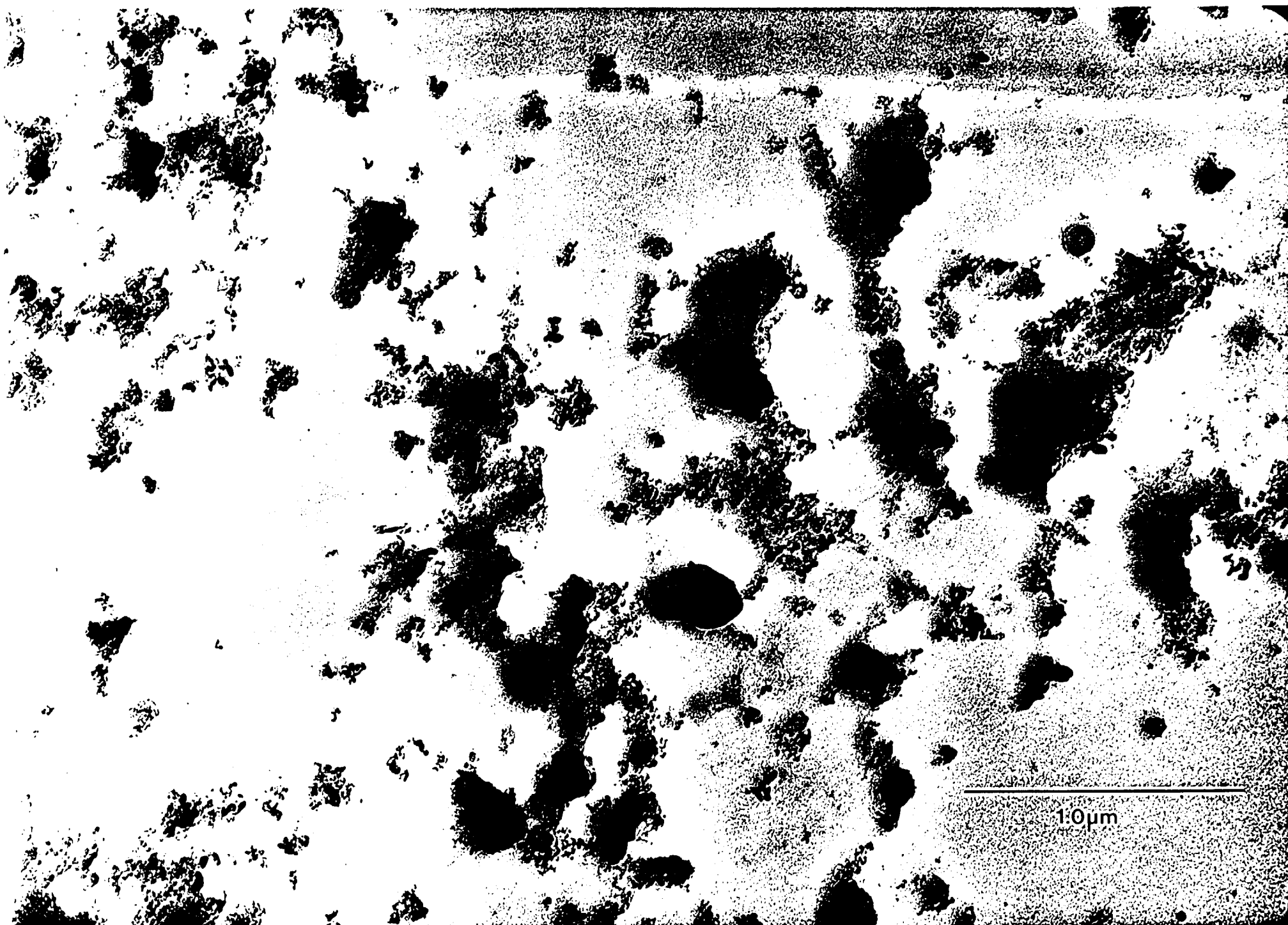


Figure 15

observed. Soot particles do not exhibit a dark spot around them on the formvar film and are easy to see in detail, suggesting that filmy coatings are not present in these particles. Figure 5 shows particles in a typical FOV from this sample.

Results of the 500-particle classification:

C-O-Si chain aggregates	239
C-O-Si solid rounded particles	187
C-O-Si blob particles	13
C-O-Si, with S	4
Low Counts particles	26
Sulfate particles (S-O)	19
Sulfate with Na, K, and/or Cl	2
Si-rich	10

Flight 6/25/97 Sample #13 – F-16 #1 – High S Fuel – 0.1-1 Nautical Mile Separation

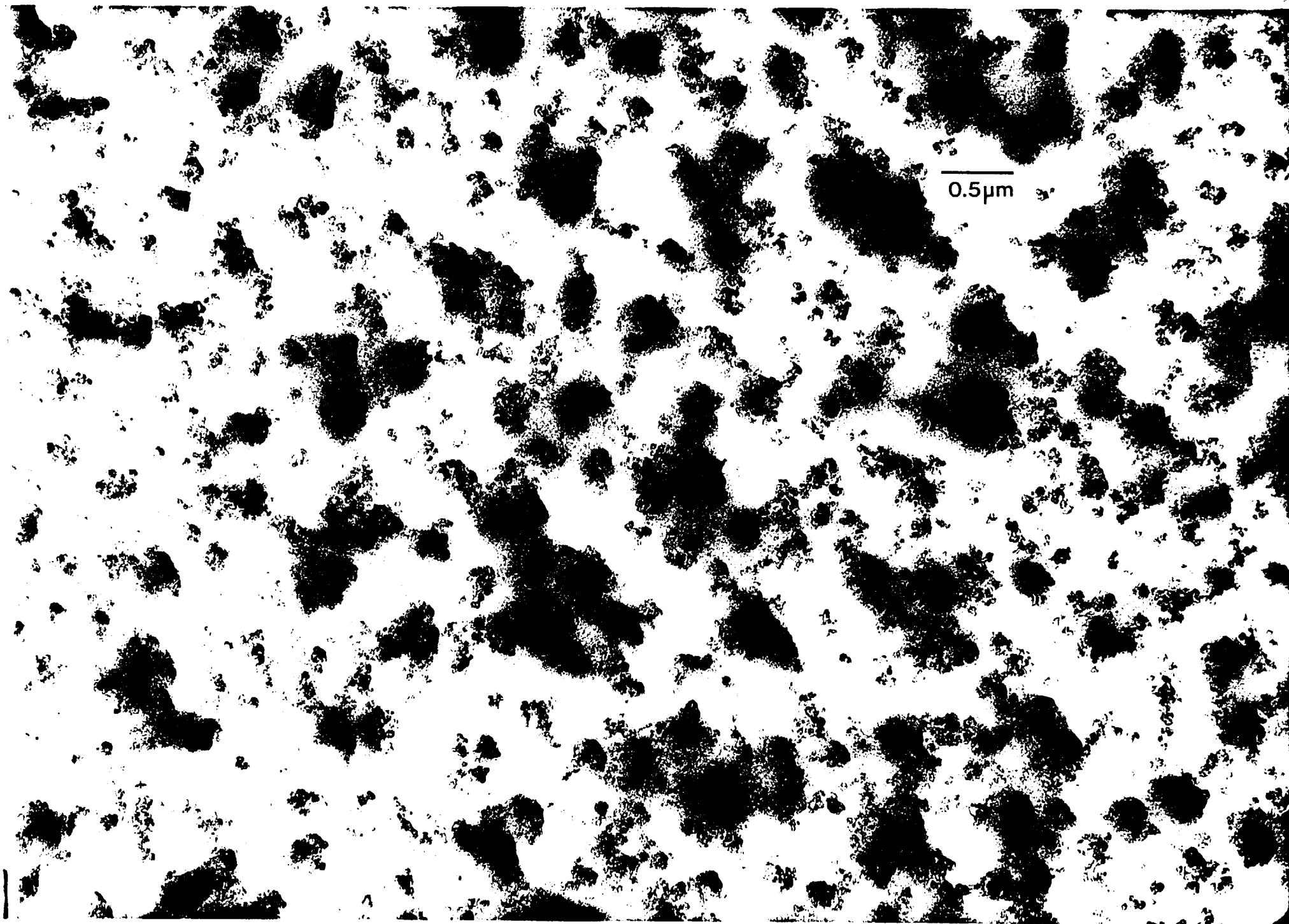
This sample contains lots of soot particles and a good CAD. The soot particles are mostly of the chain aggregate type, although the other types are also present. These soot particles and aggregates often appear to be coated with a film – this has been observed on other “High-S Fuel” samples. Figure 16 and Figure 17 show more examples of particles from this sample that may have coatings that preclude sharp imaging.

Results of the 500-particle classification:

C-O-Si chain aggregates	179
C-O-Si blob particles	59
C-O-Si solid rounded particles	200
C-O-Si, with S	13
Low Counts particles	31
Sulfate particles (S-O)	9
Si-rich	7
Ti-rich	1
Fe-rich	1

Flight 6/27/97 Sample #16 – F-16 #1 – Low S Fuel – 0.1 Nautical Mile Separation

This grid displayed a very inhomogeneous deposition pattern with many of the island type of deposits. No clear-cut CAD region was observed. The vast majority of the grid squares showed



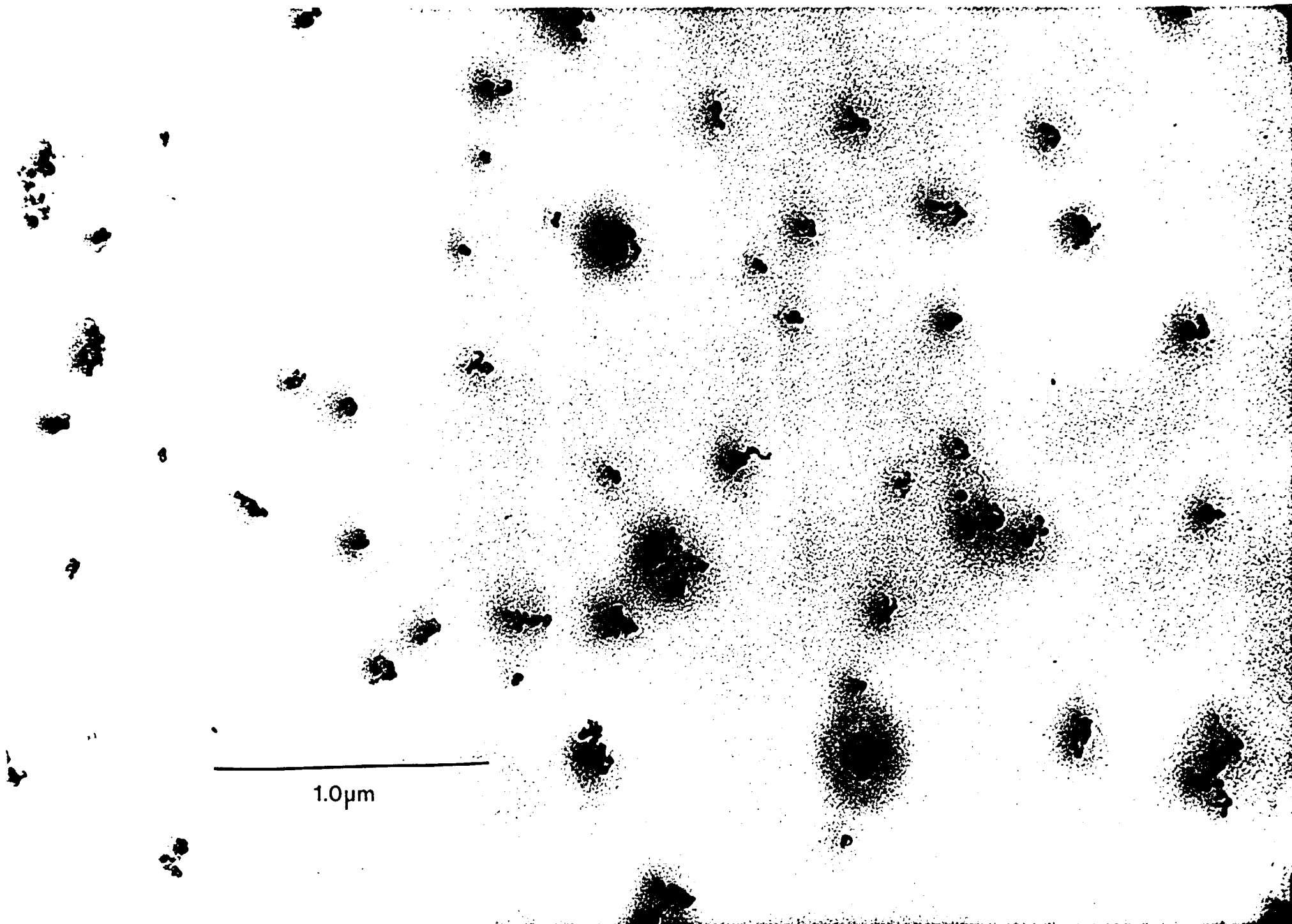


Figure 17

only a few particles present, and these low-loading squares were sometimes adjacent to deposition island squares containing hundreds to thousands of particles. We have to question whether the impactor was functioning correctly during this sample. The highly irregular deposition pattern suggests that the pre-collection substrate might be overloaded and losing material by ablation. We must also question that if this is the case, can particle analyses from areas outside the deposition islands be trusted. This grid was of the fine-mesh variety, so surface available for particle analysis was reduced dramatically. There were enough broken-film grid squares that finding 500 particles for analysis outside of the island deposits was not possible. The particles observed in the islands appeared to be soot particles primarily of the blob and solid morphologies. Relatively few chain aggregate soot particles were observed in this sample. The composition of these classes of particles was again C-O-Si.

Results of the 500-particle classification:

Not performed.

Flight 6/27/97 Sample #15 – F-16 #2 – JP-8 Fuel – 0.1 Nautical Mile Separation

This grid was also not handled well – it could however be straightened for analysis. This sample also showed highly uneven deposits and no clear CAD area, but there were sufficient particles outside of the “islands” to conduct a 500-particle analysis. Particles were a mix of chain aggregates, blobs, and small solid C-O-Si types. Si was often higher than expected in these particles, occasionally in the 20-30% mass fraction range. Trace elements were sometimes observed in these soot particles. Some sulfate particles were observed, but not many relative to the soot particles. Metallic particles of several types were found occasionally, as were salt-like particles.

The soot particles did not appear to have any sort of residue or filmy coating associated with them. This has been observed before in previous samples from JP-8-fueled engines (e.g., Flight 6/25/97, Sample #14). Analysis of particles in the deposition island areas frequently showed high Si. The highest Si mass fractions (occasionally reaching 25%) were found in the large agglomerate masses in these deposition islands.

Results of the 500-particle classification:

C-O-Si solid rounded particles	165
C-O-Si chain aggregates	79
C-O-Si blob particles	129
C-O-Si, with S	3
Low Counts particles	31
Sulfate particles (S-O)	49
Si-rich	37
Ti-rich	4
Fe-rich	1

Al-rich	1
Crustal	1

Flight 6/27/97 Sample #14 – Background Air

Grid was severely mangled – bent up almost in a ball. It was straightened to the extent possible and analyzed. This caused much of the formvar film covering the grid squares to break. This grid shows uneven deposits and no obvious CAD region. Most squares are lightly loaded with particles (5-10 per square), and there are a few heavy-deposit squares dispersed among them. As usual, there are a lot of soot particles on this grid, but most of these appear to be of the solid type rather than chain aggregates. We must decide whether these particles are aged, compacted soot particles from the atmosphere or whether they've been knocked off the pre-impaction surface. Many of the C-O-Si particles in this sample also contain Na, K, Cl, or S. The soot often appears as blobs, and nearly all of the soot particles have darker residue spots around them. This makes it difficult to obtain clear images of the soot particles.

Results of the 500-particle classification:

C-O-Si solid rounded particles	215
C-O-Si chain aggregates	29
C-O-Si blob particles	99
C-O-Si, with minor S	21
C-O-Si, with minor Na, K, or Cl	45
Low Counts particles	18
Sulfate particles (S-O)	48
Si-rich	14
Ti-rich	1
Fe-rich	2
Cr-rich with minor Na, K	1
Cr-rich with minor Fe	2
Na-, Cl-rich	2
K-, Cl-rich	1
Crustal	2

VI. Discussion

In this section we summarize and attempt to explain the observations documented in previous sections of the report. These explanations are full of conjecture and speculation; they were

intended be that way and to elicit discussion among the PIs. Obviously, before we "go public" with our results we have to be sure we understand what it is we're measuring and whether sampling problems caused some of our data to be unreliable. Hopefully, the questions that are asked will provide the stimulus for answers from our group rather than evoking more questions.

The major observations from the TEM grid analyses are summarized below.

- 1) Aircraft exhaust particles were observed in a variety of morphologies ranging from classic chain aggregate soot particles to "amorphous blob" particles that may have impacted in a wet, moist or dual-phase state. Some samples showed blob particles that looked like they could have been coated chain aggregates. Regardless of their physical appearance, the particles generally showed similar compositions of 60-90% C, 2-10% O, and one to several percent Si, with trace elements occasionally observed. Oxygen was rarely present above a 10% mass fraction, but Si occasionally was observed at the 20-30% (by mass) level. Higher Si mass fractions were usually observed during bulk analysis of larger agglomerate masses.
- 2) Soot particles in some samples appeared blurred under high-resolution observation. We proposed that they were covered with a thin film or coating that made viewing and obtaining images of these particles difficult. These coatings were not explicitly visible during analysis. Darker spots that may be residue from these films were usually present around these soot particles. Analysis of the residue spots showed no large differences in composition from the soot particles. This has not been observed before in similar samples analyzed during previous NASA programs. The blurred particles appear to be more prevalent in samples collected at very close sampling distances, although this was not a consistent finding.
- 3) Some of the samples showed uneven particle deposition patterns in place of or in addition to a central aerosol deposit. These uneven patterns appeared as "deposition islands" of high particle numbers superimposed on a lower-loading background. The composition of particles in these high-loading areas was essentially the same as for particles in other areas of the grids, although occasionally Si was present in higher amounts.
- 4) Particles emitted from C-130 and F-16 aircraft are very similar in composition, but often are morphologically quite different. The C-130 exhaust is characterized by more C-O-Si blob particles and less solid or chain aggregate soot particles. The exhaust of F-16 aircraft appears to contain a higher fraction of solid and chain aggregate soot particles. Samples from both of these aircraft usually showed little or no detectable S on exhaust particles, even in cases where high-S fuel was being consumed. Samples collected at a close following distance showed very few sulfate particles; the relative number fraction of sulfate particles increased with larger following distances.
- 5) "Background air" samples showed higher than expected numbers of soot particles in addition to acidic sulfate particles.

We need to ask ourselves if there could be an important difference between the blob and chain aggregate soot particles that merits making a distinction between the two, since they have essentially the same elemental composition. This is not necessarily the same as saying they are made of the same material, because much of the C in the blob particles could be in an organic form. Obviously, chain aggregates can account for a lot more surface area per unit mass than rounded particles, so this is a potential reason to keep the distinction. Could morphology of the

soot particles be used as an indicator of fuel or lubricant composition, combustion temperature or engine conditions? Is it even useful at all to attempt to count the soot and other particles, if they could possibly break into smaller fragments upon collection? Why do we consistently see Si in the exhaust particles? Is this an effect of using Si-containing fuels or lubricants in the engines of military aircraft? Will soot particles in the atmosphere with a significant mass fraction of Si absorb radiation in substantially different amounts than pure C soot particles?

The distinction we have made between chain aggregate soot and solid rounded soot is probably too fine. Solid rounded soot particles are very likely either small fragments of chain aggregates or the primary spherules before aggregation occurred. It is also possible that they are the compacted soot aggregates after atmospheric processing and aging. If so, we should simply combine the two categories into a solid soot category. We can do this at a later time if necessary. Similarly, there appears to be a gradient between the "amorphous blob" and the "solid" morphologies. While some particles clearly fall into either category, others are not so easy to classify. This classification was in some cases pretty subjective (a particle may have looked more like it belonged in one class as opposed to another). After further discussion among the PIs, we may decide to abandon the morphology distinction altogether.

The question of whether or not there is a film or coating on some of the soot particles is a difficult one to get a definitive answer for. Why do particles and edge features in some samples (e.g., 6/19/97 #22, 6/25/97 #18, etc.) appear blurry and difficult to obtain sharp images? Is there some sort of film (possibly organic) present that coats the impaction substrate and the particles on it? This appears to be more of a problem at very close sampling distances. The particles appear blurred under standard TEM viewing mode and also are usually surrounded by a darker spot on the formvar film. This could be a residue from liquid that seeped off the particle onto the film. The composition of the blurred particles and the darker spots is similar to all the other soot particles in this study (i.e., no additional trace elements are present or vastly different C-O-Si ratios observed). If a film or liquid was on the particles, our guess is that it is some sort of sticky or viscous organic fluid whose C-rich nature would not change the composition of the particles very much. A potentially similar deposit was observed in Flight 6/19/97, Sample #23, which was collected at a close distance behind a C-130 aircraft. The CAD region of this grid was covered with what looks like a solidified, originally liquid deposit of the C-O-Si composition (Figure 12). The major question here is how the liquid material (if that's what it is) could have existed in the exhaust plume and moved into the impactor. Could this deposit have resulted from the condensation of organic vapors in the impactor? Perhaps it occurred from the coagulation of many thousands of the "blob"-type C-O-Si particles?

Another question centers on how the uneven particulate deposits occurred. There is no doubt that some samples showed a central aerosol deposit of particles that decreased in loading with increasing radial distance from the impactor jet. This is how we expect this single jet impactor to deposit particles. The suspect samples show "deposition islands" of high particle loading spread around the grid and surrounded by low-loading areas. It is our hypothesis that clumps of material from the pre-collection surface (designed to remove particles $> \sim 0.2 \mu\text{m}$) were loosened and blown back to the collection substrate. This effect was worse at some times than others, possibly influenced by changes in the impactor operating pressure, jet velocity, or size of the pre-collection deposit. We have to question whether particle analyses on grids that show this effect should be considered valid. None of the 500 particles analyzed during the formal counting portion of the grid analysis was from any of the deposition island squares. Still, we have to ask

how likely it is that large clumps would be the only particles blown off the forward impaction surface. Some small aggregate particles and even individual particles may have existed on the pre-collection surface and could have changed chemically or morphologically before becoming airborne again. Of course, particles that did come from the pre-collection surface are still largely aircraft soot from this sampling program, and compositional information is probably still valid. Particle morphology would probably be the least valid of the observed particle characteristics, and relative abundances of the various particle types could be skewed.

Another question we have to ask is whether the distance from the aircraft that the sample was collected has any relationship to particle composition, morphology, or relative abundance. This study suggests that relative abundances might be affected by sampling distance behind the engine. Very few sulfate particles were observed in samples collected at close distances behind an aircraft. This probably reflects the relative lack of sulfate particles in the near-exhaust plumes, and the likelihood that gaseous S compounds did not condense onto exhaust particles over these short distances and times. As distance behind the sampled aircraft increased, the collected particles in many samples showed a larger number fraction of sulfate. This is either because S had enough time to get onto exhaust particles in the plume, or that dispersion and mixing of the exhaust into the background air brought sulfate particles into the sampling path. Small soot particles were observed in or on sulfate particles in samples where sulfate particles were plentiful.

It is unknown why so many soot particles were observed in "background air" samples 6/19/97 #19 and 6/27/97 #14. We can speculate on two possible reasons. One possibility is that the sampling location was not entirely in background air (i.e., the altitude that was sampled experienced recent aircraft activity or a dispersing aircraft exhaust plume was intercepted). The other prospect we have identified is that the soot came from a heavily-loaded pre-collection surface or the impactor walls. We must ask whether the impactor was periodically cleaned over the duration of the program. If not, then this second possibility becomes more likely. We may have no representative background aerosol samples with which to compare the exhaust samples.

With respect to our analytical resolution, we emphasize that we can routinely observe solid C-rich particles in the 10-20 nm range during our 500-particle counting/sizing analyses. Significantly better resolution is possible with this microscope, but changing magnifications and optimizing the instrument for higher resolution work is time consuming and labor intensive. Sulfuric acid particles, which lose mass in the electron microscope and leave a residue on the thin film, are visible when the spread spot exceeds $\sim 0.03 \mu\text{m}$ in diameter. As stated above, the minimum particle size for obtaining elemental compositions is somewhat larger. Figure 18 shows a FOV showing both C-rich and H_2SO_4 particles from one of the background air samples (970619, #19). This photomicrograph is included as an example of both the routine resolution of our microscope during the 500-particle counting process and the predominance of external mixing of sulfate and soot particles that was observed throughout this study. If 20-nm soot particles had routinely existed within sulfate particles in these samples, most would likely have been observed and documented as such.

It is our hope that the data presented and the questions raised in this report lead to timely discussion among the Principals of this study. It is imperative that we proceed with this discussion as soon as possible given the other studies that are being published on this topic. Personally, the author would like to see conference calls set up for this purpose, but email correspondences would also be fine. Ideas are encouraged for any new methods for

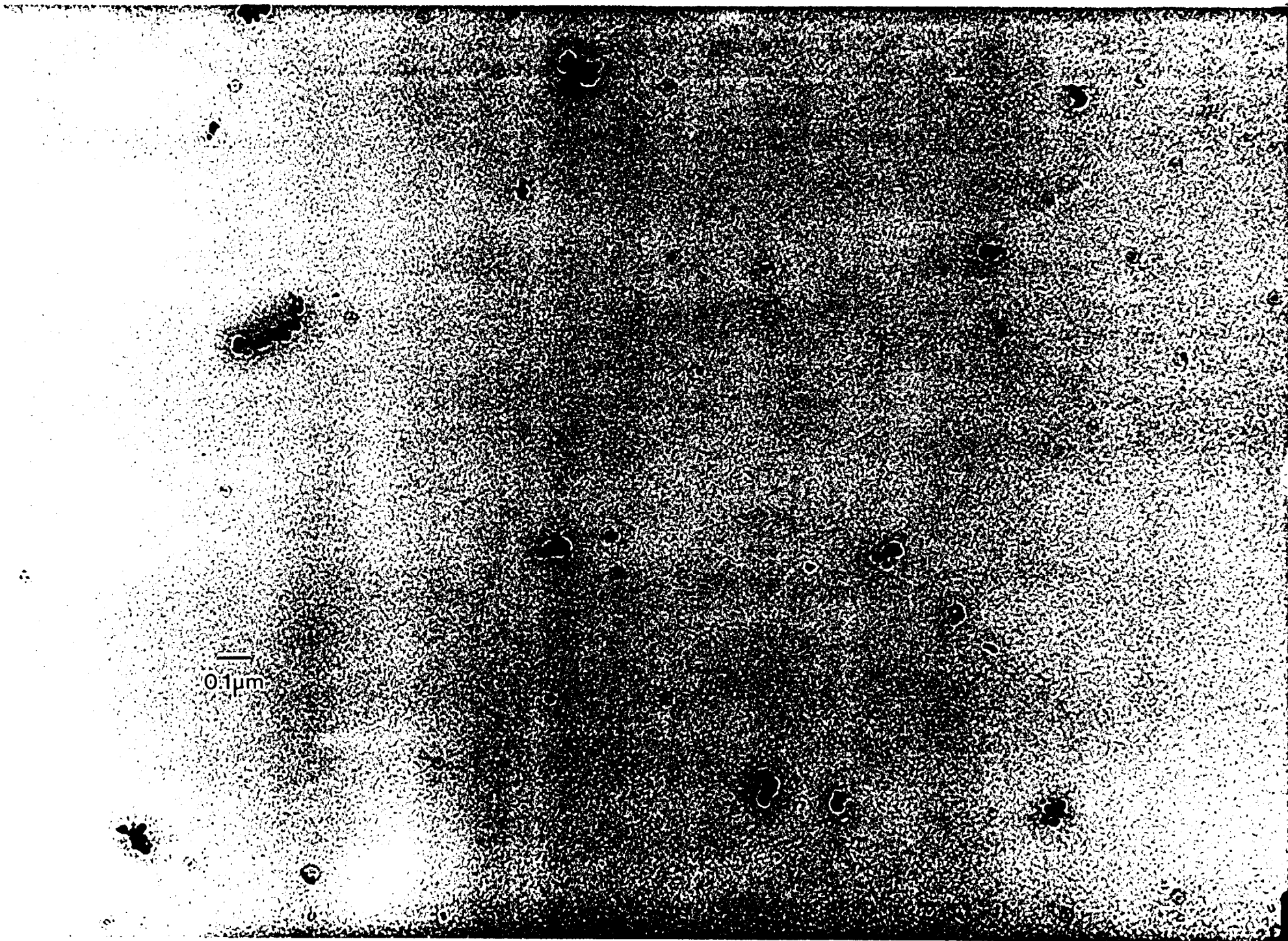


Figure 18

microanalysis that might give us more information than we are getting with the current techniques. Also encouraged is input from each of the PIs addressing the questions that were raised during the analyses (even if the answer to the question is "I don't feel that's an important point to dwell on"), especially those dealing with impactor operation (e.g., collection efficiency and uneven deposition patterns). If we can't trust the impactor, perhaps we can't believe all the data!

Some of the questions raised in this report may not be answerable without laboratory work designed to better characterize impactor performance and collection efficiency. If deemed necessary, these studies should be undertaken at the earliest convenience. Remember that all samples have been archived so re-analysis of some of these samples is possible.

